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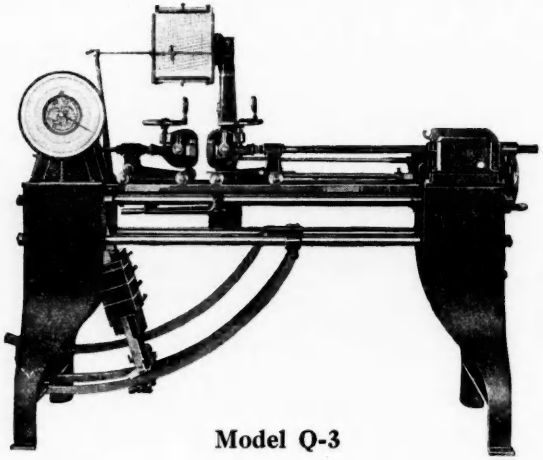

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Some Mechanical Factors Influencing Size Application

By WILLIAM E. YELLAND*

A Research of U. S. Institute for Textile Research, Inc.

Summary

Results presented in this article indicate that (1) at higher slashing speeds warps of 150 denier 40 filament bright viscose pick up less size than at lower speeds when the warp is completely immersed in the size mix by means of an immersion roll.

(2) The use of a blanket on the squeeze roll (or of fewer weights on the squeeze roll) causes more size to be taken up by the warp than when the squeeze roll is bare. No difference in size distribution on the yarn was detected in this case. The use of a blanket on the squeeze roll also increases the drying requirements of the warp.

Introduction

IN previous articles it has been mentioned that among the mechanical factors which influence the application of size are the speed of slashing and the condition of the squeeze roll; that is, whether the roll is blanketed or bare and what pressure is applied to it. During the course of experiments investigating other phases of slashing there have been collected observations and data which relate to these factors, and which are presented in this article.

Speed of Slashing

Experiments on 150 denier 40 filament bright viscose rayon tend to show that less size is picked up at higher than at lower speeds. A typical example is given here. The standard speed of slashing for warps of a certain construction was 40 yards per minute. Toward the end of a warp, slashed at this rate, the speed of the slasher was decreased and the last few hundred yards were sized at the rate of 20 yards per minute. No other settings on the slasher were changed. When the warp had woven sufficiently far in the loom, samples were taken at various places according

* Dr. Yelland was director at Massachusetts Institute of Technology of the filament viscose rayon phase of the warp sizing research from Jan. 1, 1936, to Sept. 30, 1938, and is now with Corn Products Refining Co., Research Laboratory, Edgewater, N. J.

to the method described in a previous article (TEXT. RSCH., Aug. 1940, *10*, P. 420–424) and the size content was determined as usual.

Results showed that at lower speed the warp had taken up one-fifth more size than at the higher speeds. This is evident from the following table:

Speed	% Size	Average % Size
40 yds. a minute.....	3.04, 2.92, 3.04	3.00
20 yds. a minute.....	3.68, 3.56, 3.52	3.59

At this point the effect of the way in which the warp is drawn through the size box and quetsch must be considered. The technique in use at the mill where these experiments were carried out was as follows: The warp was drawn from the single warp beam, which had been made up on the silk system, and passed over a drag roll. Then it entered the size mix and went under an immersion roll. Leaving the size mix the warp next passed through the nip of the quetsch and squeeze rolls, and went finally to the drying cans. The length of time that the warp was actually in the size box was determined by the depth to which the immersion roll was adjusted and the speed of slashing. If the first factor remained unchanged then the higher the slashing speed the shorter the time of immersion of the warp in the size would be. Under these circumstances it would be expected that less size would be picked up at higher speeds.

Although not used in this series of experiments there is another technique employed by mills in which the warp is not immersed in the size mix at all but passes directly from the drag roll through the nip of the quetsch and squeeze rolls. In this case the size liquor is carried up to the warp by the lower roll which revolves partly immersed in the size. The amount of size taken up by the warp then depends in part on how much size liquor is carried up to the warp by the roll. At higher speeds more size would tend to be carried up and consequently more size would be picked up by the warp. It was not feasible to carry out the experiments necessary to demonstrate this point in this research program. However, it has been confirmed by reliable reports and observations from other mills.

The relationship of size pick-up to slashing speed has been an important factor when new high-speed slashers have been installed in place of old equipment. Mills have found it necessary to adjust the per cent solids in the size mix to compensate for the effect of increase of speed on the amount of size taken up by the warp. Since the size content of the warp is affected to such an extent by the slashing speed it is obvious that for most uniform results the speed should be maintained as constant as possible.

Squeeze Roll

The question has frequently been raised as to whether the function of the squeeze roll is to squeeze size into the yarn (that is, to cause the size to penetrate between the filaments) or to squeeze the excess size and moisture out of the warp, or both. This can be answered best by examination of cross-sections of yarn under the microscope for size distribution. Not enough samples have been studied to answer this question conclusively; but no difference in size distribution could be observed in these experiments when cross-sections of the warp ends were stained and examined under the microscope.

However, it may be stated that changes in the squeezing pressure exerted by the roll have at least two important results, namely: (1) In changing the amount of size taken up by the warp. (2) In changing the drying requirements of the warp.

The changes in the squeezing pressure of the roll may be brought about either by covering the roll with a blanket or by decreasing the weights on the compound quetsch lever. Either of these procedures decreases the pressure exerted by the roll on the warp yarn.

Two warps of the same construction were slashed as follows: (1) With the usual blanket on the squeeze roll. (2) With the squeeze roll bare.

Size determinations gave the following results:

Condition of Roll	% Size	Average % Size
Blanketed	5.2, 5.5	5.3
Bare Rubber	3.7, 3.9	3.8

This is a comparatively large change in size content and would affect the weaving properties of the warp markedly. A similar but not so evident change occurs gradually as the blanket on the squeeze roll ages. A new blanket is not packed down so firmly on the roll and consequently it gives a lighter squeeze to the yarn and leaves more size in the warp. As the blanket is used it becomes denser, the yarn is squeezed harder and less size is left in the warp.

There are disadvantages in the use of either the bare rubber roll or the blanketed roll. If the surface of the rubber roll becomes grooved or otherwise worn irregularly the roll must be removed from the slasher for grinding, whereas a blanket can be changed readily. The efficiency of the blanket is variable, however, since it depends on the age of the blanket and the care with which it is wound on the roll. Moreover, a blanket has a marked tendency to aggravate foaming in the size box. This is especially true with acetate yarns where the finish on the yarn may cause considerable foaming.

The drying requirements of warps were discussed in more detail in a previous article. [TEXT. RSCH., Oct. 1940, *10*, P. 526–530.] However, it may be pointed out here that, when the heavy squeeze was used, only the first four out of seven drying cans were necessary to dry the warp to approximately 9% regain. When the lighter squeeze was used, six drying cans were necessary to bring the warp to the same regain, using the same steam pressure in the cans as before.

Simplified Method for the Determination of Refractive Indices of Textile Fibres

By KENNETH R. FOX * and ROGERS B. FINCH †

A Textile Foundation Publication

Abstract

A new method of determining the refractive indices of fibres is described which uses as its basis, a photometric match of Becke line intensities emanating from the difference between the maximum and the minimum refractive indices of the fibre and the index of the mounting fluid.

Introduction

THE optical properties of textile fibres as indicated by their respective indices and particularly the specific index of birefringence are progressively augmenting the current knowledge of fibre structure. In addition, the molecular orientation of fibres under known conditions of stress [1] or strain can be correlated with the birefringence thus opening up a field of research directly applicable to the stresses and strains experienced in textile processing. The double variation method for determining the refractive indices of textile fibres [2] was presented at an earlier date but it was felt by those who were in intimate contact with the procedure that a more satisfactory method might be developed which would simplify the technique. The present project was started with this in mind and it has proved to be more simple and time-saving as well as opening new fields of investigation beyond the limitations of the double variation method.

Theory

An optical phenomenon described in the literature as the Becke line serves as the basis for this method. Such authors as Chamot and Mason,[3] Johannsen,[4] J. M. Preston,[5] and E. R. Schwarz [6] have reported the presence of this line and in some cases have endeavored to explain the optics involved. Suffice it to say at this stage, that the line apparently is formed by the refraction and reinforcement of certain light rays when crossing boundaries between two media of different refractive indices. If a fibre is immersed in a fluid of a lower refractive index and viewed through a microscope, a bright line called the Becke line appearing on the edge of the fibre will be seen to move toward the fibre when focussing up from sharp focus. And conversely, if the fluid index is higher than the fibre index, the bright line will be seen to

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Research conducted under the direction of Prof. Edward R. Schwarz.

move toward the fluid. In other words, the bright line moves toward the medium of higher refractive index when focussing up from sharp focus.

All textile fibres are anisotropic, i.e., they possess more than one refractive index. In order to measure these unidirectional properties, plane polarized light rather than heterogeneous light must be used to isolate these indices. The index along the fibre axis (N_γ) is measured when the fibre is oriented parallel to the plane of polarization, whereas the index transverse to the fibre axis (N_α) is measured when the fibre is oriented perpendicular to the plane of polarization. This former position will be designated as the γ position while the latter will be called the α position. Now if a fluid possessing a refractive index *between* the N_γ and the $N\alpha$ of the fibre is selected, the following observations can be made.

When the fibre is oriented in the γ position, the bright line will be seen to move into the fibre but if the fibre is rotated to the α position by turning the revolving stage of the microscope through 90°, the bright line will now move into the fluid. In effect, a reversal of the bright line movement can be noted by merely rotating the fibre through 90°. These conditions are represented in Fig. 1. From the result of experimentation, it was noticed that the brightness of the Becke line at any one position was governed by the proximity of the fluid index to the fibre index. It was also noted that when rotating through 90°, the Becke line inside the fibre in the γ position did not disappear until the Becke line outside the fibre in the α position appeared. It is possible, then, to obtain some fibre position where the Becke lines are both visible and photometrically matched. The magnitude of the angle through which the fibre must be rotated to reach this match is governed by the magnitude of the fluid index relative to the indices of the fibre. It is this relationship of angle, fluid index, and fibre indices that has been investigated and is presented in the following discussion.

Apparatus

The source of illumination * used in the present equipment consists of a carbon arc lamp with a clock-work feed. Although this feed is not entirely automatic, it does avoid the necessity of constant adjustment of the carbons as they burn. This light then passes through a heat absorbing water cell to the monochromator. This piece of apparatus consists of a wave-length spectrometer used in conjunction with a shutter eyepiece to control the spectral purity of the lines selected. The direct-reading wave-length drum is an essential feature of this instrument since any desired wave-length of light can be obtained rather quickly and easily. Monochromatic light is necessary in obtaining refractive indices of liquids and hence of solids by the immersion technique, as both of these media exhibit chromatic dispersion. The light emanating from the monochromatic source passes either directly to the microscope or it can be directed to the refractometer by means of mirrors.

The microscope is equipped with a built-in substage polarizer and graduated rotating stage. The rotating stage is necessary in order to rotate the fibre into the position of photometric match of Becke line intensities. A special constant temperature stage plate through which water is circulated to maintain the immersion fluid and specimen at any known temperature is used with the microscope. This stage was designed so as to avoid any tendency for air bubbles to form as well as to produce a smooth flow, free from

* The equipment is now in the process of rearrangement utilizing a sodium arc which eliminates many of the past difficulties experienced with the carbon arc and the monochromator.

any discontinuities. The temperature of the water is controlled by a special heater and control unit able to give a steady flow through the microscope and refractometer at a specified temperature. Since the index of a fluid varies with temperature (thermal dispersion), it is necessary to have the temperature of the fluid in both the mount and the refractometer substantially the same in order to avoid a false reading of the mounting fluid index.

The refractometer is of the Abbé type equipped with water-jacketed prisms but without the customary Amici compensating prisms. The omission of these prisms was considered desirable in view of the fact that a slight deviation from parallelism of the prisms leads to a small error in the index readings. The refractometer used is calibrated for sodium light but as sodium light ($\lambda = 589\ m\mu$) was used for all observations, no correction curve is necessary.

To facilitate the reading of the index scale on the refractometer, a lamp housing is attached to the quadrant of the refractometer. Thus, the bulb

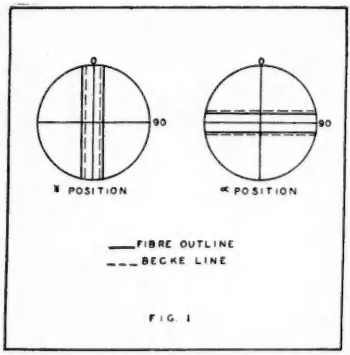


FIG. 1

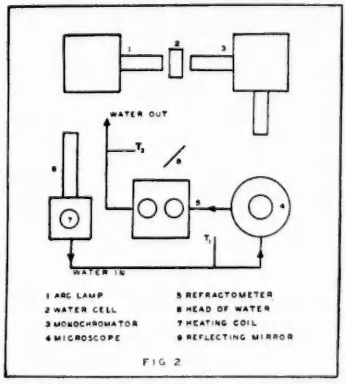


FIG. 2

illuminating the index scale will remain in a fixed position relative to the eye-lens regardless of the position of the movable arm. It is of paramount importance to insure that the fluid temperatures on the stage and in the microscope are in sufficient agreement not to exceed the refractometer sensitivity. From repeated tests it was found that the thermal dispersion of the range of fluids used was of the order of 0.0005 for one degree Centigrade. As the refractometer uncertainty is $\pm$ 0.0002, a temperature differential between the two fluids of 0.4° C. can be used and not exceed the instrument limitation. Recognizing this fact, thermometers reading in tenths were inserted in the circulating water before the microscope and after the refractometer so that this differential in temperature could be checked during each test. The rubber tubing used for the circulating water is suspended above the equipment so that the stage of the microscope can be rotated free from tubing entanglements. A schematic diagram of the equipment is shown in Fig. 2.

Because the refractive index measurements are made at fairly low intensities of illumination, it was found best to conduct such tests inside a special wooden housing to inclose the apparatus and the observer. The

housing is painted a flat black within and is covered on the observer's side by a curtain. A dome light within the housing serves for general illumination for the purpose of reading the graduated stage and noting data.

Immersion Fluids

Before any measurements can be made, it is necessary to choose a fluid possessing an index between the n_γ and the n_α of the fibre being tested. These fibre indices can be found listed in many standard text-books but quite a complete list is tabulated by Herzog and Heerman.[7] In order to obtain the required fluids, it is suggested that a range of standard fluids possessing known indices be made available. The set of fluids used in this work was made up by Lappé [9] as a part of a thesis conducted at M. I. T. during 1934. His set includes thirty-one bottles of different concentrations of alpha-monochlornapthalene and 300° F. boiling point kerosene distillate.

This set of fluids has many desirable features as suggested by Butler [8]:

a) Adjacent liquids have closely identical optical properties other than index. Therefore, all properties are closely a linear function of composition with the increment other than index a minimum.

b) Any two liquids are miscible and the index of any intermediate member is a straight line function of its composition.

c) The liquids are permanent, i.e., retain constant properties under all laboratory conditions.

d) Solid matter does not settle out on standing.

e) The mixtures are clear, colorless, non-poisonous, and free from objectionable odors.

f) The liquids do not react chemically with each other nor with the substances tested.

Schwarz [10] corroborates the advantage of having fluids whose index is a simple function of composition, so that

$$n = \frac{n_1 v_1 + n_2 v_2}{v_1 + v_2}$$

where

n = index
v = volume.

This relationship presents a simple means of fluid mixing in order to approximate a desired index of the mixture.

The following table lists the indices of the standard solutions at the wave-length used for all observations.

Effect of Immersion and Temperature Equilibrium Time

Textile fibres are not inert physically or optically to certain fluids and so the effect of immersion upon the optical properties must be standardized before any one reading can be taken. Any change in the indices of a fibre would be reflected in the angle at which the Becke lines are photometrically matched. Several runs were made upon viscose * rayon in order to determine the effect of the mounting fluid over a period of time. In order to obtain sufficient data, observations were made at two minute intervals and the

* Viscose rayon was chosen because it is moderately birefringent and possesses a relatively high regain.

Refractive Indices of Standards

Bottle	$(n)^D$ 20° C.	Bottle	$(n)^D$ 20° C.
1	1.4509	16	1.5280
2	1.4559	17	1.5327
3	1.4612	18	1.5378
4	1.4664	19	1.5431
5	1.4716	20	1.5476
6	1.4766	21	1.5528
7	1.4812	22	1.5581
8	1.4861	23	1.5628
9	1.4922	24	1.5681
10	1.4971	25	1.5730
11	1.5020	26	1.5773
12	1.5072	27	1.5831
13	1.5122	28	1.5874
14	1.5179	29	1.5928
15	1.5228	30	1.5978
		31	1.6026

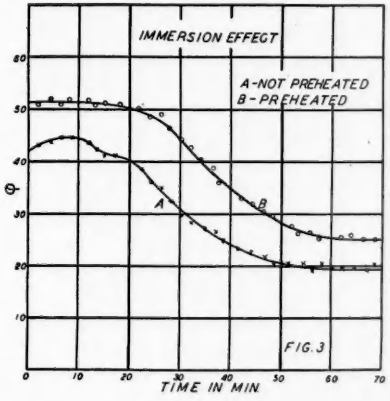
n of kerosene = 1.4500^D 20.0° C.
n of α monochlornaphthalene = 1.6317^D 20.0° C.

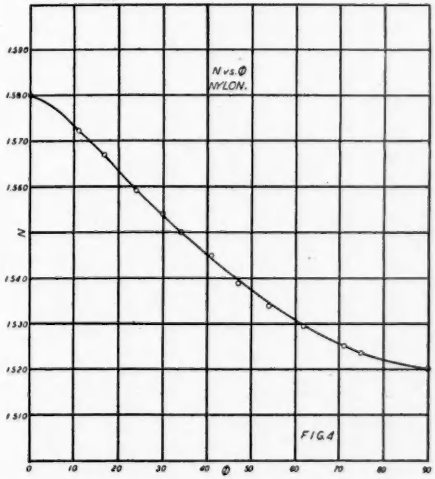
resulting angle recorded. See Fig. 3. It may be stated here that initial equilibrium appears to be maintained for at least twenty minutes and the effect of immersion does not evidence itself until after this time. If any readings are taken upon a fibre within this time, no error caused by the effect of immersion will be involved. Readings taken upon other fibres appear to substantiate this as well. After a period of two hours all fibres appeared to have reached a point of saturation. The authors feel that much more information must be gathered about the relation of immersion and optical properties, particularly the effect of immersion on form anisotropy, before any dogmatic statements can be made.

While investigating the effect of immersion, it was found that there was considerable variation in the initial readings. Because the first few readings were taken before there was an opportunity for the cover glass, the fibres, and the immersion medium to come to the temperature of the hot stage, it was suspected that the initial temperature differentials involved were causing these variations. From curve A, Fig. 3, it may be seen that these variations occurred during the first ten minutes. In order to overcome this effect, the fluid was placed upon the center of the stage and the cover glass and fibre placed to one side of the stage. This procedure allowed the liquid, fibre, and cover glass to come to temperature equilibrium independently. After ten minutes, the fibres were mounted in the liquid and the cover glass placed over them. It was found that no variations occurred and the regular immersion picture resulted. (Curve B.) For purposes of diagram simplification the run represented by curve B is shown at a higher temperature, hence the larger values of φ. This preheating, therefore, is an essential part of the technique of obtaining the angles of photometric match.

The preheating method can be still simplified by storing the fluids, cover glasses, and fibres to be tested in an oven set at the temperature of the circulating water. However, the ultimate arrangement is one in which all the observations can be made in a room with rigidly controlled temperature

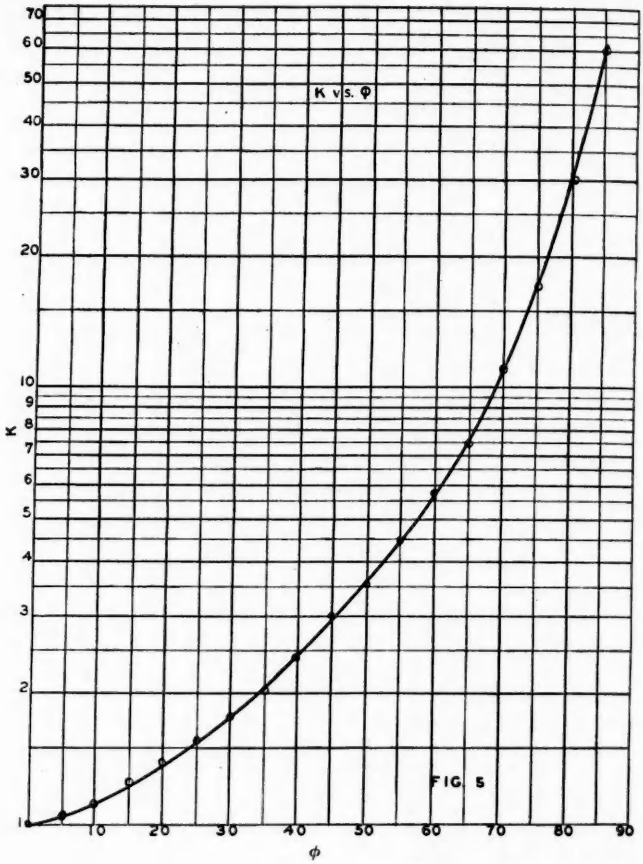
conditions. If this is done, even the circulating water can be omitted. It is then possible to prepare a mount immediately and the angles can be read in less than a minute.





Mathematical Correlation of Data

In the theory, it was stated that if a fluid possessing an index between the N_γ and N_α of the fibre be selected, the Becke line in the γ position will move toward the fibre and in the α position will move toward the fluid. It



was also noted that the intensity of the Becke line at any one position was governed by the difference between the fibre and fluid indices.

From the foregoing, the following line of reasoning can be employed. In the γ position, the difference between the fibre and fluid indices (n) is proportional to $(n_\gamma - n)$ while in the α position, the difference is proportional to $(n - n_\alpha)$. The actual sign of these expressions has no significance as only those fluids with indices between n_γ and n_α are used. Both expressions, in this case, will be positive in sign at all times so that only positive numbers will occur in the final expression.

If a fibre is rotated from either the γ or the α position through some angle β, the intensity of the Becke line will diminish until the line disappears.

At any angle β_1, measured from the γ position, the Becke line intensity may be expressed in terms of the fibre index in that position (n_{β_1}) and the index of the fluid (n) by the expression ($n_{\beta_1} - n$). The ratio of the intensities of the line at $\beta = 0$ and $\beta = \beta_1$ may, therefore, be expressed as a function of β_1, namely

$$\frac{n_\gamma - n}{n_{\beta_1} - n} = f(\beta_1)$$

For the same reason, with an angle β_2 measured from the α position and $\beta = 90$ and $\beta = \beta_2$

$$\frac{n - n_\alpha}{n_{\beta_2} - n} = f(\beta_2)$$

The most useful position of the fibre is that at which the γ-line and α-line are photometrically matched. This point of match may be found most accurately between 20° and 70° for it has been found that this is the region of best comparative Becke line definition. At this point

$$\beta_2 = 90 - \beta_1$$

and

$$n_{\beta_1} = n_{\beta_2}$$

The combined expression in terms of n_γ, n_α, n, and β_1 now becomes

$$\frac{n_\gamma - n}{n - n_\alpha} = \frac{f(\beta_1)}{f(90 - \beta_1)} = f(\beta_1)$$

The angle φ measured from the γ position will be used hereafter to designate the special condition of β_1 where the γ-line and the α-line are matched. Substituting φ for β_1, the expression becomes

$$\frac{n_\gamma - n}{n - n_\alpha} = f(\varphi)$$

In attempting to evaluate this function, a series of values of n versus the corresponding values of φ for nylon * were taken and plotted (Fig. 4). As it is quite difficult to obtain the angles below 20° and above 70°, the end points, i.e., n_γ and n_α, were checked by two observers using the longer double variation method. It was found that a smooth curve through these points corresponded in shape but not in degree to a mathematical curve of n versus φ as determined from the equation of an ellipse. This theoretically derived curve must be modified by the function $\tan^2 \varphi$ (the function which describes the ratio of the intensities of illumination between the two planes of polarization). The mathematical solution of this $f(\varphi)$ was found to be so involved and unwieldy that it was abandoned in favor of a simpler and more useful empirically derived expression.

The curve of n versus φ for nylon was taken as the basis for this expression. Values of

$$K = \left[\left(\frac{n_\gamma - n}{n - n_\alpha}\right) + 1\right]$$

versus φ were plotted on semi-logarithmic coordinates as shown in Fig. 5. The formula representing the ratio of the Becke line intensities can now be

* Nylon was chosen because it is strongly birefringent and so offers a wide latitude for well defined angle measurements.

written as

$$\frac{n_\gamma - n}{n - n_\alpha} = K - 1$$

By using this formula in conjunction with two values of K and the corresponding indices, n_γ and n_α can be determined for any fibre. The use of $K - 1 = f(\varphi)$ rather than $K = f(\varphi)$ facilitated plotting K versus φ and produced simpler resulting formulae.

Solving the two following equations simultaneously

$$\frac{n_\gamma - n_1}{n_1 - n_\alpha} = K_1 - 1$$

and

$$\frac{n_\gamma - n_2}{n_2 - n_\alpha} = K_2 - 1$$

gives:

$$n_\alpha = \frac{K_2 n_2 - K_1 n_1}{K_2 - K_1} \tag{1}$$

$$n_\gamma = K_1 n_1 - n_\alpha(K_1 - 1)$$

or

$$n_\gamma = K_2 n_2 - n_\alpha(K_2 - 1) \tag{2}$$

$$n_\gamma - n_\alpha = \frac{K_1 K_2}{K_2 - K_1}(n_1 - n_2) \tag{3}$$

By using a strongly birefringent fibre, nylon, to obtain the K values, the region of maximum variation was investigated. If the K values are adapted to fibres of weaker birefringence, these variations are minimized.

The following example will illustrate the use of the formulae.

Viscose filaments were immersed in two fluids and the corresponding angles with the K values read from the curve are as follows:

$$n_1 = 1.5380 \qquad \varphi_1 = 25 \qquad K_1 = 1.55$$
$$n_2 = 1.5265 \qquad \varphi_2 = 57 \qquad K_2 = 4.86$$

Substituting in the formulae gives

$$n_\alpha = \frac{4.86 \times 1.5265 - 1.55 \times 1.5380}{4.86 - 1.55} = 1.521 \tag{1}$$

$$n_\gamma = 1.55 \times 1.5380 - 1.521(1.55 - 1) = 1.547 \tag{2}$$

$$n_\gamma - n_\alpha = \frac{1.55 \times 4.86}{4.86 - 1.55}(1.5380 - 1.5265) = 0.026 \tag{3}$$

Further results of determinations made upon weakly, moderately, and strongly birefringent fibres are tabulated below.

Fibre	n_γ	n_α	$n_\gamma - n_\alpha$
Acetate Rayon	1.478	1.473	0.005
Wool	1.556	1.547	0.009
Viscose Rayon	1.547	1.521	0.026
Silk	1.591	1.538	0.053
Nylon	1.580	1.520	0.060

It was found that fibres not only varied among themselves but also at adjacent points on the same fibre. Bearing this in mind, ten observations on different fibres were made to obtain a figure more adequately depicting the actual indices. The values quoted above were obtained in this manner.

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Combination of Wool Protein with Acid and Base: The Effect of Temperature on the Titration Curve

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Abstract

A description has previously been given of the relation between the amounts of hydrochloric acid and of potassium hydroxide bound by wool and the concentration of these substances in solution. These measurements were made at 0° C in order to avoid complications due to decomposition. However, when wool is exposed to acid or base in the course of carbonizing, acid-dyeing, milling, and scouring much more elevated temperatures prevail. It is therefore desirable to determine the temperature dependence of the relations previously described. It is also desirable to compare the relative magnitudes of the effect of temperature on the amounts of acid and on the amounts of base combined, in order to establish the correctness of assumptions as to the mechanism of combination previously made in explaining the results obtained at 0° C.

With the purpose of providing this information, measurements of the amounts of hydrochloric acid and potassium hydroxide bound by wool as a function of acidity and salt concentration, at 0°, 25° and 50° C, are now reported. In order to eliminate effects due to decomposition of the wool in alkaline solutions, a study was also made of the effect of temperature on the rate of decomposition of the wool. The results obtained support the assumption previously made that the carboxyl groups and amino groups of wool in the uncombined state are completely ionized. This conclusion follows from the observation that changes in the amounts of acid bound brought about by changes in temperature are small, which indicates that combination with acid is equivalent to back-titration of the carboxyl groups, but changes in the amounts of base bound at at given hydrogen ion concentration are large, which indicates that combination with base is equivalent to back-titration of amino groups. Similar results obtained on analogous compounds, render it probable that the direction of the temperature effect on the curve of acid combination reverses at a temperature near 40° C. Thus curves at temperatures used in dyeing are probably not far different from the curves at 0° C, which have been studied in most detail.

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The heats of dissociation calculated from the magnitudes of the changes with temperature in the curves of combination for the two kinds of groups, are in good agreement with values for these groups in comparable compounds, and in soluble proteins. The value obtained in the acid range is also in good agreement with the results of calorimetric measurements on the combination of acid by wool.

It is shown that approximately equal parts of the total heat changes in the acid range are associated with the dissociation of hydrogen ions and of chloride ions from the fibre. An appreciable part of the total heat effect is ascribed to a heat of transfer of the ions between the two phases of the heterogeneous titration system. Neither titrimetric nor calorimetric estimations of the heats of dissociation provides evidence for or against the existence of salt linkages in wool.

Introduction

MEASUREMENTS of the dependence on pH and salt concentration of the amounts of hydrochloric acide and potassium hydroxide bound by wool at 0° have been described in an earlier publication by two of the present authors.[19] * The proposed theoretical analysis of these measurements was based on the assumptions (1) that in the uncombined state the carboxyl groups and basic groups are completely ionized, i.e., the hydrogen atoms of the carboxyl groups have been transferred, with their positive charges, to the amino and guanidino groups, leaving negatively charged carboxylate groups and positively charged alkylammonium groups; (2) that when the protein combines with hydrogen ions it also forms partially dissociated stoichiometric complexes with negative ions, (e.g., Cl^-), and when it combines with hydroxyl ions, it forms similar complexes with positive ions (e.g., K^+). The first assumption is equivalent to postulating for the protein the same zwitterion † structure originally proposed for amino-acids and certain other ampholytes by Adams [1] and by Bjerrum [2] and now almost universally adopted as the result of the researches of Bjerrum,[2] Harris and Birch,[15] Wyman,[35] Cohn and his collaborators,[7] and others. The purpose of the present paper is to adduce evidence justifying application of the dipolar ion concept to wool protein. Experiments designed further to justify and extend the second and less familiar assumption are at present in preparation for publication.

It was pointed out by Bjerrum [2] that the effects of temperature on the dissociation constants of the α-amino-acids furnished an indication of their existence as dipolar ions. Since the publication of Bjerrum's paper this criterion has been made use of in the study of proteins as well as of amino-acids by Pertzoff and Carpenter (casein),[24] and by Wyman (hemoglobin).[36] Changes in temperature were observed to have very small effects on the parts of the titration curves of these proteins which lie on the acid side of neutrality, but the effects on the alkaline side were very considerable. These results may be understood if these proteins are, like their constituent amino-acids, dipolar ions, since then the addition of alkali to their solutions serves mainly to remove hydrogen ions from amino groups, the dissociation constants of which are very dependent upon temperature.

* Figures indicate the literature references at the end of this paper.

† In the remainder of this paper the term "dipolar ion" is substituted for "zwitterion" in conformity with recent American usage.[6, 7]

Measurements of the effects of temperature on the titration curves of wool keratin, presented in the present paper, lead to the same conclusion. They also offer a means of evaluating the energy changes accompanying the associations of anions and cations, postulated in assumption 2. It is a consequence of this assumption that the anions of different acids should be characterized by different affinities for wool (i.e., this affinity is inversely related to the degree to which they dissociate under standard conditions).* The existence of these postulated differences in affinity would be manifested by different positions with respect to the pH coordinates of the titration curves of wool obtained with different acids.† The differences in affinity, if sufficiently large, would be accompanied by varying degrees of sensitivity of the respective titration curves to changes in temperature. While an inverse relation between the magnitudes of dissociation constants and the heats of the corresponding dissociations is not regular or exact, it is so general that the demonstration of an increased temperature dependence of the titration curve with ions of high affinity should be an essential part of the experimental validation of the second assumption. Because of the wide use of hydrochloric acid by all investigators of the acidic and basic properties of wool as well as of other proteins, and because the data with this acid are unusually complete, it is convenient to refer all comparisons of the titration curves of wool with other acids to the common basis of its titration curve with hydrochloric acid, and to express the affinities of the anions of other acids in terms of the affinity of wool for chloride ions. For this purpose one needs not only titration data with hydrochloric acid at a single temperature, such as have already been described,[29] but also measurements of the effect of temperature on the same equilibrium, as given in the present papers. In order to obtain accurate data in solutions of alkaline pH, at which decomposition of the disulfide bonds occurs very very rapidly at room temperature, it has also been necessary to investigate the lability of this bond as a function of temperature as well as of pH and concentration of ions.

Irrespective of what views may be entertained as to the nature of the equilibria involved in the titration of wool with acid or base, it is desirable to appraise any effect which may be produced on the normal temperature dependence of a protein titration curve by the circumstance that the titration system exists in two phases. With this information at hand it should be possible to determine the relationship of the detailed titration measurements previously obtain at 0° C to the phenomena of combination of acid and base by wool at the elevated temperatures which prevail when wool is exposed to acid or base during carbonizing, acid-dyeing, scouring, and milling. If an effort is to be made to relate the equilibria in such a process as acid-dyeing to the acid-base equilibrium between wool and an inorganic acid, the latter must be defined at the temperature at which the process in question is normally carried out.

Experimental Procedure

Details of the preparation of materials and of most of the methods used in the present investigation have already been described.[29] Modifications in

* It has been demonstrated[28, 30] that very wide differences do indeed exist between the affinities of the anions of various acids for wool, and for other proteins.

† In the case of acid dyes this affinity is directly related to fastness to washing and to alkalies.

the procedures, or considerations bearing on their applicability to measurements made at high temperatures are listed in the following subsections:

1. Materials

In order to assure that data obtained at different temperatures might be legitimately compared, most of the measurements were made on a single large batch of root wool fibres, purified as previously described,[29] and carefully mixed before the final carding to insure homogeneity. Thus, certain of the measurements previously made at 0° C with a different batch of wool have been repeated, and use has been made of the earlier measurements at this temperature only in certain cases in which a number of duplicate measurements with the new batch of wool showed the essential identity of the two sets of results. On incineration at 700° C the wool used left an ash of 0.26 per cent; the hydrogen ion equivalence of its cation content, as shown by electrodialysis,[28] was 0.036 millimole per g. Measurements of the amounts of acid or base bound have been corrected for the alkali equivalence of the ash by subtracting from or adding to the measured acid or base bound an amount, 0.032 millimole per g. determined by direct comparison with the wool containing only a negligible amount of ash used in the previous investigations,[29] as well as by subtracting the average amounts of chloride removed from solution in a large number of measurements from the average amount of hydrogen ion taken up in the same series. The closeness of the empirical correction, 0.032 to the equivalence of the cationic ash, 0.036, shows that the larger part of the cations are combined with the fibers as base, and are not present as adsorbed or entrained inorganic salts. Although the amount of ash is small, and due allowance has been made for its alkali equivalence in calculating the amounts of acid or base bound by wool free of ash, it must be recognized that the presence of an alkaline ash in the fibres results in the introduction of small amounts of salt into all the acid solutions, including those to which no salt was intentionally added. Thus, curves obtained with acid in the absence of added salt may nevertheless show small effects characteristic of the presence of traces of added negative ions,[29] especially in the pH region where very small amounts of acid are combined.

2. Methods

(*a*) *Titration with Acid*

Hydrolysis of amide groups from glutamine and asparagine residues contained in the protein was considerably more rapid at 40° and 50° C than at the lower temperatures previously reported. This extent of hydrolysis was minimized by limiting the time of immersion of the wool to approximately 24 hours, an interval which proved sufficient for attainment of equilibrium at 25° C and at higher temperatures. Even in this shorter time, however, sufficient hydrolysis occurred to require the application of corrections for the ammonia produced. Thus, at 50° C, 0.5 *M* hydrochloric acid liberated approximately 0.12 millimole per g of wool and 0.2 *M* acid liberated 0.035 millimole per g of wool per day. The presence of salt (potassium chloride) increased these rates. In addition to ammonia, very small amounts of other soluble products were formed at 40° C and 50° C, as evidenced by the weak positive biuret test given by the solutions. With

the concentrations of acid used, the biuret test was always negative in experiments at temperatures below 25° C, even after periods of immersion up to four or five days. The appearance of soluble, peptide-like decomposition products at higher temperatures is probably not accompanied by any appreciable increase in the number of basic groups in the insoluble residue, since no increase in the maximum combining power of wool for acid is found at 50° C over the value for 0° C previously reported, when corrections are properly applied for the effects of the hydrolytic production of ammonia.* The presence of dissolved fragments of protein in the aliquots titrated should be without effect on measurements of the acid taken up by the protein when indicators having endpoints well on the acid side of neutrality are employed in the necessary titrations.

(*b*) *Titration with Base*

Harris and Rutherford have shown [16] that when wool is exposed to alkaline solutions, disruption of its disulfide bonds results in the more or less rapid formation *in the fibre* of groups which combine with base (tentatively identified as sulfhydryl), and that the number of acid groups which are formed in this manner approaches as a limit the number of cystine residues initially present. At the same time half of the sulfur originally contained in the cystine is found in solution as inorganic sulfide. By determining the dissolved inorganic sulfide and applying additional small corrections for the wool dissolved [20] an estimate can be made of the extent of decomposition of the disulfide linkages. It is an empirical fact that at all temperatures reported in this paper, increases in the amounts of base bound, as a function of time of exposure to alkaline solutions, closely parallel the production of dissolved sulfide. This finding, originally reported for 0° C by Harris and Rutherford, provides a basis for distinguishing between the additional base bound by acid groups formed as the result of decomposition at any temperature, and the base that is bound by the residual unmodified protein. The application of this correction merely requires subtraction of the number of equivalents of sulfur split off per gram of wool from the total amount of base neutralized per gram in the same experiment.† This procedure clearly involves the assumption that the newly formed acid groups are sufficiently strong to combine *quantitatively* with base at the pH values at which disulfide breakdown occurs. At 0° C and at 25° C the range of pH in which appreciable quantities of inorganic sulfide are found in solution is sufficiently high, especially when data are obtained in the absence of added salt, so that this assumption is not called into question, even when it is postulated that the groups formed are the very weakly acid sulfhydryl, formed by hydrolysis of the disulfide bonds.[5, 16] The dissociation constant at 25° C of the sulfhydryl group of cysteine itself is not far from 10^{-10} [4], and practically quantitative combinations of this acidic group with base can be expected at pH values above 12. In the presence of 0.2 *M* potassium ions at 25° C little sulfur is split out within

* The reported increase in the capacity of wool to bind hydrochloric acid at high temperatures [10] may be explained by the failure to take into account the production of ammonia and its effect on the titers of the aliquots used in obtaining the measurements. The causes of the effects observed by the same investigators with dye acids are undoubtedly more complex.

† A slight modification of this correction, required when large amounts of wool are dissolved, takes account of the contribution of the dissolved wool to the total inorganic sulfide in solution.[20]

24 hours at pH values below 12, and in the absence of added salt practically no decomposition occurs at pH values below 12.5. At lower temperatures the pH range in which decomposition occurs is even more favorable to the concept of quantitative combination with base by sulfhydryl groups having dissociation constants not far from those of the sulfhydryl in cysteine. Nothing is known of the acid strength of sulfhydryl groups in proteins, but recent work with peptides of cysteine [11] indicate that they may be expected to be stronger rather than weaker than in cysteine itself; thus, the quantitative combination with base of this group in proteins at the pH values at which the decomposition of wool occurs *at low temperatures* is a virtual certainty.

At 50° C, the evidence also indicates practically quantitative combination of the newly formed acid groups with base, but the lowest pH at which extensive decomposition is found at this temperature is very much lower than when low temperatures are used. In the presence of 0.5 *M* potassium ions, appreciable decomposition within 24 hours occurs at pH values only slightly higher than 8, and even in the absence of salt appreciable loss of sulfur within this time is found at pH values below 10. Unless the sulfhydryl groups which may be formed are more than one thousand times more acidic in the protein than in the amino-acid cysteine, it may not be assumed that stoichiometric combination between these groups and base would occur in this range of pH. Nevertheless the evidence for the occurrence of such stoichiometric combination is as strong in the measurements at 50° C as it is for the experiments at lower temperatures.

One possible alternative to attributing the necessary relatively large acid dissociation to sulfhydryl groups in the protein lies in the possibility that the newly formed acid groups may be other than sulfhydryl. Thus, for example, the sulfhydryl groups produced by the hydrolytic reaction postulated by Harris and Rutherford might be readily oxidized by air in alkaline solutions to stronger sulfur acids. No evidence at present available demonstrates conclusively the presence of appreciable quantities of free sulfhydryl in wool from which almost one-half of the initial content of sulfur has been removed by severe treatment with alkali at temperatures between 0° C and 50° C. Such wool gives little or no reaction with the nitroprusside reagent, and treatment with *p*-chlorobenzyl chloride fails to introduce significant amounts of chlorine into the fibre.* The present incomplete evidence may thus be interpreted as favoring the view that if sulfhydryl groups are initially formed, they are rapidly transformed to other radicals with more strongly acidic properties than those usually attributed to sulfhydryl groups in familiar compounds. Application to the titration data of the correction for the formation of new acid groups does not depend on speculation as to the nature of these groups but rests upon the experimental demonstration that such groups are actually produced. Details of this demonstration, already furnished by Harris and Rutherford in work at 0° C and 22°C, have been extended to measurements made at 50° C, and are indicated in part in the section that follows.

It is noteworthy that at 50° C the corrections for the protein dissolving in alkaline solutions became almost negligible because the propor-

* It has been shown [23] that when sulfhydryl groups are formed by *reduction* of the disulfide groups in wool they may be quantitatively alkylated or aralkylated with alkyl or aryl halides. By using *p*-chlorobenzyl chloride as the aralkylating agent the extent of the aralkylation may be determined by subsequent analysis of the fibres for chlorine.

tion of the total wool which dissolves at a given degree of decomposition of the disulfide bonds diminishes sharply as the temperature is increased. Thus, for example, under conditions causing the splitting of 25 per cent of the disulfide bonds after a day of exposure to alkali at different temperatures, it is found that approximately 3.0 per cent of the fibre has dissolved at 0° C, only 1.5 per cent has dissolved at 25° C, and less than 0.8 per cent has dissolved at 50° C. This effect, which might appear contrary to the usual effect of temperature on solubility, is readily understood on considering the pH values at which the same given degree of decomposition of the disulfide bonds takes place in 24 hours at the three temperatures—pH 14.1 at 0°C, pH 12.4 at 25° C, and pH 9.3 at 50° C. It thus appears that the dissolving of wool in alkaline solutions does not depend solely on the combination of the newly formed acid groups with base, but that a large proportion of the pre-existing groups in the fiber which undergo acidic dissociations in alkaline solutions (largely RNH_3+ groups for lysine and arginine) must react with base before dissolution occurs. (The removal of a hydrogen ion from RNH_3+ groups increases the net negative charge of the protein as effectively as the conization of a carboxyl group.) This conclusion is supported by the way in which the amount of wool dissolved depends on pH at the three temperatures. At each temperature the amount dissolved per disulfide bond broken is practically constant (at the level indicated by the preceding figures) until at least one-quarter of the disulfide bonds have been disrupted. Beyond a certain pH characteristic of each temperature this constancy no longer prevails, and the amount dissolving per additional disulfide bond broken increases rapidly. At 0° C, this critical pH is approximately 14, at which value between 30 and 40 per cent of the cystine has been destroyed; at 25° C the rapid increase in solubility begins at about pH 13, at which value, however, over 60 per cent of the cystine has broken down; at 50° C the sharp rise in solubility occurs near pH 11.6 after 80 per cent of the initial content of cystine has been lost. The differences between these pH values, *which do not correspond to the decomposition of a definite proportion of the disulfide bonds in the protein,* is approximately the same as the differences between the position of the titration curves along the pH axis at the same temperatures. Since in these ranges of pH, the curve is largely determined by the equilibrium $RNH_3^+ + OH^- \rightleftharpoons RNH_2 + H_2O$, it seems probable that the dissolution of wool requires the combination with base of a large proportion of the pre-existing, as well as of the newly formed, acidic groups. It should thus be possible, by treating wool at elevated temperatures with solutions only slightly to the alkaline side of neutrality, to destroy practically all the disulfide bonds in its structure without dissolving an appreciable amount of the fibers.

(*c*) *Measurement of pH*

The accuracy of the pH measurements between pH 7 and pH 10 was improved by calibrating the glass electrode with .05 *M* sodium tetraborate at all of the temperatures at which measurements were made, in addition to employing the other pH standards already enumerated.[20] The value, 9.180, given by Hitchcock and Taylor[17] for 25° C, was used as the basis for calculating the pH values of this buffer at 50° C, from the ratio of the dissociation constants of boric acid at 50° C and 25° C as given by Owen.[21, 22] The same procedure was used in determining the pH value of this buffer

for 0° C, but an extrapolated value of the dissociation constant was employed, since Owen's data do not extend below 5° C. The values employed in standardizing the electrode were 9.39 at 0°C, 9.18 at 25° C, 9.07 at 40° C and 9.04 at 50° C.

By employing a standard in this range of pH, in which the glass electrode starts to deviate from the theoretical behavior of a perfect hydrogen electrode, it was possible to obtain more nearly exact correction terms for the pH measurements made in solutions above pH 9, than when the correction was averaged over the long interval between the pH of phthalate buffer and that of the dilute potassium hydroxide solution previously described. All determinations of pH values above 5.5 were made at the temperature at which the titration curves were measured. Control measurements showed that pH measurements at room temperature could be substituted for measurements at the temperature of the experiment at pH values below 5.5.

(*d*) *Control of Temperature*

The thermostatic equipment previously described kept the temperature constant within ± 0.1° C and 0° C, within ± 0.02°C at 25° C, within ± 0.1° C at 40° C and within ± 0.5° C at 50° C.

3. Results and Discussion

Measurements of the combination of wool with both hydrochloric acid and potassium hydroxide as a function of pH were made at 0° C, 25° C, and 50° C. Sets of measurements were made with solutions which contained no added salt, and with solutions to which a neutral salt, potassium chloride, had been added in quantities sufficient to maintain predetermined constant concentrations of chloride ions in the experiments with acid, and constant concentrations of potassium ions in the experiments with base. Two constant ionic concentrations, 0.2 *M* and 0.5 *M* were used. A fourth temperature, 40° C, was included among those at which measurements of combination with acid were made in the series of solutions to which no salt was added, and 25° was omitted from the temperatures at which measurements were made in solutions of 0.5 *M* ionic strength. The results obtained in the three different sets of measurements are represented graphically in figures 1, 2, and 3, in each of which results obtained at different temperatures in a given ionic environment are directly compared. In each figure, the points on the alkaline side of neutrality connected by the broken curves represent measurements of base bound calculated in the accustomed way,[29] from determinations of changes in the titer of alkaline solutions in which samples of wool have been immersed for approximately 24 hours. The points immediately above each of these, connected by the solid curves, represent the same measurements after application of the corrections for the effects of disulfide breakdown discussed in Section 2. The necessity of making corrections for disulfide hydrolysis when working at temperatures near 0° and 25° C has already been demonstrated.[29] The present measurements show that the errors which would be introduced by neglecting to take disulfide hydrolysis into account are even more serious at 50° C than at the lower temperatures. Thus, the positions of the broken curves, representing measurements made after 24 hours, are in part fortuitous and depend in a high degree on the length of time during which the wool is

immersed in the experimental solutions. Points representing the corrected measurements, however, always fall on or near the appropriate solid curve, regardless of the time elapsing before the solutions are sampled, provided that sufficient time has been allowed for attainment of equilibrium. These statements are illustrated by sets of measurements, represented by crosses, made after the wool has been immersed in the experimental solutions for three or four hours in place of the longer period. The lower of each pair of two crosses at the same pH, shows the calculated amount of base combined when no account is taken of the base bound by acid groups formed in the fibre as the result of hydrolysis of disulfide bonds; the upper cross represents the same measurement properly corrected. The crosses representing the corrected measurements all fall very slightly above the solid curves, which

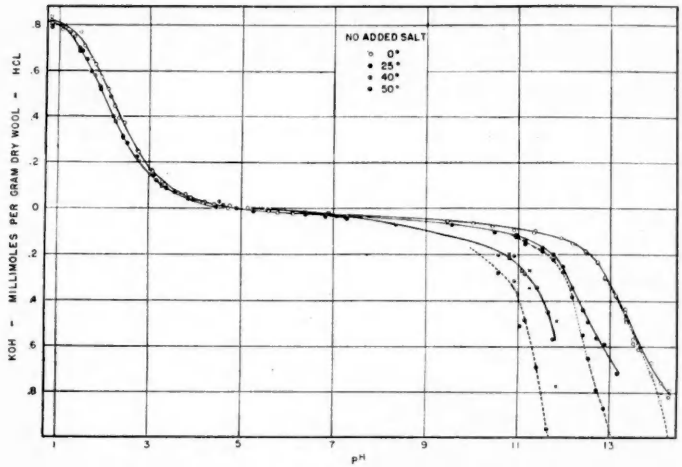

Fig. 1. Combination of wool with hydrochloric acid and with potassium hydroxide as a function of pH and temperature, in the absence of added salt. The difference between the solid lines and the broken lines is explained in the text.

indicates that the time allowed was somewhat short of that required for the attainment of equilibrium. Since less decomposition occurs in the shorter time interval, the uncorrected measurements lie considerably higher than the corresponding broken curves, and relatively much closer to the corrected data. It is clear that the corrections applied to the data obtained in alkaline solutions yield a much closer approximation to measurement of an acid-base equilibrium which is independent of time than do the uncorrected data, and that it is the corrected rather than the uncorrected data which should be used in the comparison of the results obtained at different temperatures.

It is apparent that the rate of decomposition increases sharply as the temperature is raised. Thus, it can be seen in Fig. 1, representing measurements made after 24 hours, that only negligible amounts of decomposition occur at 0° C at pH values up to 13.5. At 25° C practically all the di-

sulfide bonds are hydrolyzed at this pH within the same interval of time. At this temperature, considerable decomposition within 24 hours cannot be detected at pH values below 12.1, at which pH value decomposition is again practically complete at 50° C within the same period of time. Comparable large differences between the rates of decomposition at each of the same temperatures can be seen in figs. 2 and 3.

The principal qualitative features of the comparison of the data obtained at different temperatures are common to all three sets. They are most readily distinguished in figure 1 in which the steepness of the titration curves obtained in the absence of salt results in a sharp distinction between the positions on the pH axis of the curves obtained at each temperature. It is apparent on inspection that the curves represented are rela-

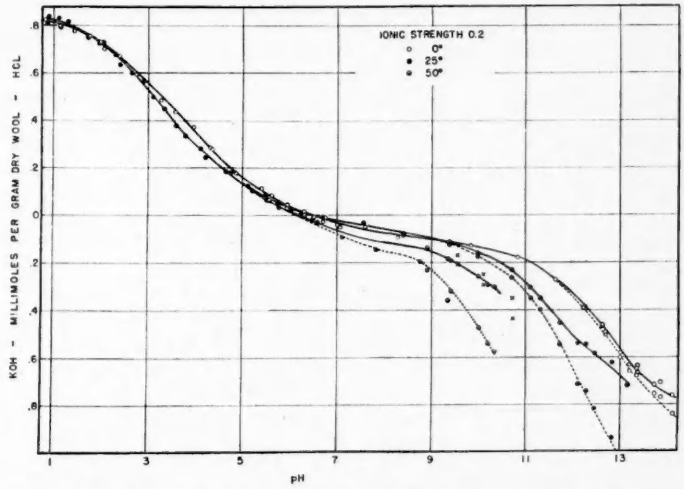

Fig. 2. Combination of wool with hydrochloric acid and with potassium hydroxide as a function of pH and temperature, at 0.2 M ionic strength.

tively well-separated with respect to position on the pH axis at the alkaline end of the scale (reference is here had to the solid curves), but that their positions differ only very slightly in neutral and acid regions of pH. Indeed, the separation between the curves of acid-combination is so small in the temperature interval, 25° C to 50° C, that only a single curve has been drawn through the points representing measurements made at 25° C, 40° C, and 50° C. Between 0° C and 25° C, however, an appreciable difference in the position of the curves is found; it is in the same direction as the shift recorded in the alkaline range of pH, but it is a good deal smaller. In the intermediate range of pH values the differences in the positions of the titration-curves are more difficult to evaluate, because of the very large change in pH which is required to produce a small increment in acid or base bound, and because pH measurements are less accurate in the extremely unbuffered solutions in this region of pH. The best estimates

which can be made from the figure indicate a shift in the abscissae of the points in the same direction as in the other parts of the curves, as the temperature is increased. This shift is intermediate in magnitude between the small effect in the acid region and the much larger effect in the most alkaline range. Its exact magnitude is so uncertain, however, that no effort is made to evaluate it in the sections that follow.

The flatness of the titration curve determined in the absence of salt also renders the precise pH value at which neither hydrochloric acid nor potassium hydroxide is bound rather uncertain. In an earlier paper, the opinion was ventured that this value was probably very nearly the same in the absence of salt as in its presence, approximately 6.4. More numerous determinations in this region now make it appear that *in the absence of*

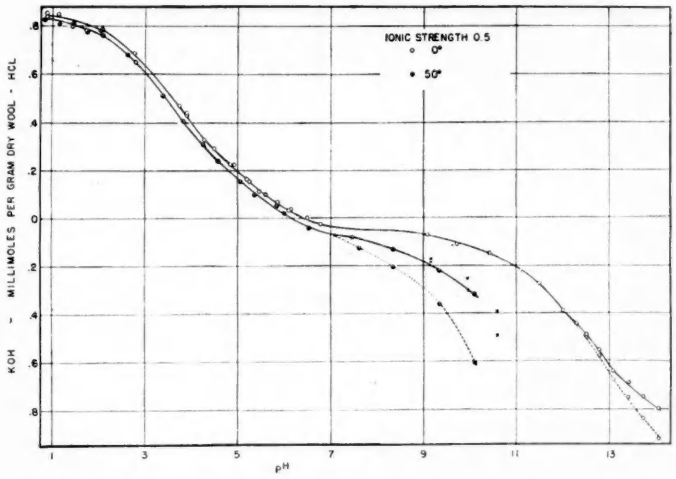

Fig. 3. Combination of wool with hydrochloric acid and with potassium hydroxide, as a function of pH and temperature, at 0.5 M ionic strength.

salt, the pH at zero combination is in the range 4.7–5.1 where it has been placed by Speakman and others.

The well-marked differences in the relative magnitudes of the effects of temperature on the three main parts of the titration curves appear to be as characteristic of proteins, as of their constituent amino-acids, as the recalculation of the data of Hoffman and Gortner on casein by Pertzoff and Carpenter,[18, 24] and the work of Wyman on horse hemoglobin [38] have shown. They are entirely consistent with the assumption previously made that the carboxyl and amino groups of the uncombined protein are completely ionized. The effect of temperature on the acid branch of the titration curve is small because the heats of dissociation of carboxyl groups are, in general, very small. The values for different carboxylic acids are distributed about zero, so that the sign of the heat may be either positive or negative, depending on the identity of the carboxylic acid in question,

and on the temperature. The changes in heat content accompanying the dissociation of hydrogen ions from the conjugate acids of imidazole and substituted ammonium bases are, on the contrary, very considerable: some 6000 calories in the case of imidazole groups and from 9000 to 14,000 calories in the case of amino groups.[5] The values of the heats of dissociation of certain of the groups in wool may be estimated from the differences in the abscissae of the curves represented in the figure. This is done for the two main regions of the titration curve on either side of neutrality, in the discussion that follows. No effort is made to treat separately the effect of temperature in the neutral region for the reasons already given, and because the amount of imidazole groups (from histidine) in wool is known to be very small.[31]

Data Obtained in the Absence of Salt

(*a*) *Combination with Acid*

The existence of an appreciable difference between the positions of the acid combination curves at 0° and 25° C, combined with the absence of any clearly distinguishable differences between the curves at 25°, 40° and 50°, probably is an indication that the dissociation constants of the carboxyl groups of the protein attain a maximum value in the temperature interval 25°–50° C, and thus probably diminish at higher temperatures. The existence of a maximum value of the dissociation constant in the temperature range of this investigation is a common characteristic of carboxylic acids.[12, 14] For these acids the curve relating the dissociation constant to temperature has a very flat maximum, but becomes steeper (the dissociation constant acquires an increasing dependence on temperature) at temperatures farther from the temperature of the maximum.[12] The temperature of the maximum is about 25° C for formic acid and acetic acid, but diminishes as the hydrocarbon chain attached to the carboxyl group lengthens; it is not far from 10° C in the case of *n*-butyric acid.[14] A more cogent comparison is with the constants characterizing the dissociations of the carboxyl groups of the amino-acids. No maxima have been found with glycine and alanine, which have been investigated at temperatures up to 40° and 45°, respectively, but Harned and Embree have shown that with these amino-acids the variation of the dissociation constant with temperature at temperatures down to 10° C closely parallels the variation of the constants characterizing the simple aliphatic acids at lower temperatures, and indicates a maximum value of their dissociation constants at temperatures just above 40°. This is very close to the temperature of the maximum suggested by the present data.

Since the degree of dependence of the dissociation constants of carboxylic acids on temperature itself depends on temperature, little is gained by comparing the heats of dissociation of these groups in wool within any one temperature interval with similar quantities for related substances such as the amino-acids. In the interval of temperature 0° C–25° C the average heat of dissociation of the carboxyl group of glycine is practically zero, of alanine is — 450 calories, of glycylglycine and of glycylalanine is — 600; in aspartic acid, ΔH_0^{25} (the average heat of dissociation between 0° and 25° C) for the carboxyl group next to the amino group is + 1600; for the same group in glutamic acid it is + 1900. The values of ΔH_0^{25} of the γ and

δ carboxyl groups of these amino acids are 2100 and 1040 calories respectively.[5] Since the latter are the carboxyl groups which are presumably free in proteins to react with base, the acid branch of protein titration curves should be determined by the number of these groups and their properties.

Certain complications enter into the calculation of ΔH from titration data in the case of proteins, because they are polybasic. ΔH may be calculated from the shift in the abscissae of the titration curves of a monobasic acid or base, or of a polybasic acid with dissociating groups which have widely different strengths, because for such acids the difference in pH at which a given amount of base or acid is bound at two different temperatures represents the logarithm of the ratio of the dissociation constants of a single acidic or basic group $\left(\Delta pH = -\log \frac{K_2}{K_1} = -\Delta \log K\right)$.* From this change in K produced by a change in temperature, it is possible to calculate the average value of ΔH in the same interval of temperature by means of the integrated form of the Van't Hoff equation:

$$\Delta H_{T_1}^{T_2} = 4.5787 \frac{T_2 \cdot T_1}{T_2 - T_1} \cdot \Delta \log K \qquad (1)$$

The values cited above have been so calculated. It has been shown by Simms,[25] Weber,[33] von Muralt,[32] and others that the titration curves of polybasic acids which contain identical dissociating groups far enough apart from one another in the molecule to have no influence on one another's dissociation may be described by an expression which is functionally identical with the law of mass action for a monobasic acid. For such hypothetical acids, the molal ΔH per dissociating group may be calculated exactly as in the simpler cases described above, by means of the relationship $\Delta pH = -\Delta \log K$. This can even be done in certain other cases when no restriction is placed on the interrelationships of the values of all the K's, as Wyman has shown in a general and mathematically rigorous analysis of the effect of temperature on the titration curves of polybasic acids. Wyman came to the conclusion that in any region of pH in which ΔpH is practically independent of pH, ΔpH can be equated to $-\Delta \log K$ for some one dissociating group or set of groups with a good degree of approximation.† Calculation of ΔH from ΔpH in regions of transition from one constant value of ΔpH to another does not correspond to any one set of similar dissociation equilibria, and gives values intermediate to those characterizing the homogeneous sets of dissociating groups in the pH regions on either side of the region of the transition. Kern,[19, 20] Cannan,[3] two of the present authors,[29] and others, have shown that the interaction between many like dissociating groups in highly polybasic acids, such as proteins, often introduces an empirical fractional exponent (equal, or nearly equal to 0.5 and practically independent of temperature) to the hydrogen ion activity term in the simple law of mass action equation which would characterize their

* The use of pH differences and of ratios of constants avoids practically all of the theoretical difficulties that arise in attempting to evaluate the constants themselves from titration data alone. Thus ΔH can be calculated more simply and more certainly than any single value of K. The only factor left out of account in this method of calculation is the change of activity coefficients with temperature of ions other than the hydrogen ions, but the temperature dependence of such activity coefficients is known to be very small.

† Unless groups possessing distinct values of H chance to possess the same dissociation constants. In this case, the average heat of dissociation for all the groups would be given.

behavior in the hypothetical simple case. At first sight this might appear to indicate that the term $\Delta \log K$, used in calculating ΔH by means of eq 1, is not equivalent to $-\Delta pH$ (the difference in the pH coordinates of the titration curves obtained at T_2 and T_1) but is equal to ΔpH multiplied by the same empirical exponent.

Two considerations, however, show that this does not follow as a rigorous consequence of the use of the exponent. 1. The constant in the modified equation is not to be identified with the true dissociation constant of any one group or set of groups; it is a function of all the constants of all the groups, and these are widely distributed in magnitude as a result of mutual interaction. 2. It is a matter of observation that the numerical value of the empirical constant corresponds very well to the square root of the unmodified mass-law constant that might be expected to characterize the dissociation of the groups if no interaction occurred (in proteins the midpoint of the carboxyl curve comes at pH 4.2, close to the pK of carboxyl groups in polypeptides, while $-\log K$ in the empirical equation containing the exponent is 2.1). Thus the equation might well be written

$$K = k^{0.5}_{\text{monobasic}} = \frac{[H^+]^{0.5}[A]}{[HA]}.$$

From this it would follow that $\Delta \log k_{\text{monobasic}} = -\Delta pH$ and not $-0.5\ \Delta pH$.

By making the reasonable assumption that the titration curves of proteins are determined by the relative acid strengths of distinct, essentially non-overlapping sets of similar dissociating groups one may obtain values of $\Delta \log K$ in each of the two main regions of pH values of the present data for wool and compare them with similar results obtained by Pertzoff and Carpenter with casein, and by Wyman with hemoglobin. The results of this comparison, and a comparison of the corresponding values of ΔH, are given in Table 1.

It is apparent that the heat of dissociation of the acid groups of wool in the lower temperature interval is very close to the values that characterize

TABLE 1

Calculation of Average Heats of Dissociation of Carboxyl Groups in Wool and Other Proteins, in the Absence of Salt.

Protein	pH Range Studied	Temperature	$-\Delta pH$	ΔH if $-\Delta pH = \Delta \log K$
		° C.		Calories per Mol
Wool	1–5	0–25	0.16	+2380
		25–50	±0.03	±500
Horse hemoglobin	4.3–6	6.5–25		−2000 to −3000
		25–37.5		
Casein *	2–5	22–35	±0.1	±3000

* The data on casein are subject to considerably larger uncertainties than the data for the other two proteins.

carboxyl groups in dibasic amino acids, albeit slightly higher. In the higher temperature interval the heat of dissociation is very much smaller, as it must be in the region of a maximum value of K where ΔH approaches zero. The values found with casein agree with those for wool as closely as should be expected, considering the low intrinsic accuracy of the casein data, and the fact that different ranges of temperature were used. The data of Wyman for horse hemoglobin do not extend below pH 4.3, and thus cover only a small fraction of the range of the present comparison. Over this range the sign of ΔpH is opposite to that of the values of ΔpH characterizing the data for wool and indicates a *negative* heat of 2000 to 3000 calories. This difference in sign is not as important for the purpose of the present comparison as is the small magnitude of ΔH. This qualitative agreement acquires further significance when the comparison is extended to other regions of pH where the heats of dissociation of all three proteins are much larger. A possible explanation of the difference in sign between the results with wool and with hemoglobin is suggested later in this paper.

The fact that the dissociation constants of the carboxyl groups of wool have a maximum value at a temperature near 40° has an important consequence in relating the titration data reported in this paper to the acidic properties of wool at the high temperatures, near the boiling point of water, to which wool is exposed in dyeing. At these high temperatures the position of the titration curve on the pH coordinate which describes the combination of wool with acid, is probably near its position at 0°, the temperature at which the influence of various factors has been studied in greatest detail.[29]

(*b*) *Combination with Base*

On the alkaline side of neutrality, the titration curves of wool at the different temperatures are widely separated and show every indication of being nearly, if not exactly,* parallel at pH values above 10. Two nearly equal intervals with respect to the pH axis separate the curves for the three different temperatures.

In calculating values of ΔH for the acid branch of the titration curve, it was possible to proceed on the approximately valid assumption that only carboxyl groups, from aspartic and glutamic acids, determined the course of this part of the curve. On the alkaline side of the curve dissociation equilibria of two widely dissimilar basic groups, the ϵ-amino groups of lysine and the guanidino groups of arginine, as well as the dissociation of one acid group, the phenolic radical of tyrosine, may all be involved within a narrow range of pH. The relation of ΔpH to $\Delta \log K$ for any one of these sets might therefore be fairly complex. Because the curves appear to be nearly parallel over a wide range, however, one may follow the procedure justified by Wyman, substituting values of ΔpH in place of $\Delta \log K$ in eq. 1, for each interval of temperature. The results of this treatment of the data are represented in Table 2, in which it is apparent that a fairly uniform separation (probably within experimental error), and therefore a fairly constant value of ΔH, is found for the entire alkali combination curve. The values in which the greatest discrepancies appear are obtained in the region of pH in which very small amounts of base are combined. Here the curves are so nearly flat that a very small error in the measurements, or in the

* The curves were drawn freehand without attempting to make them parallel.

corrections for ash, results in large discrepancies in the pH coordinates at which these quantities of base are bound. For this reason, and because the number of imidazole groups in wool is so small as to account for only a very small amount of acid or base bound, no effort is made to evaluate ΔH in the intermediate range of pH values near neutrality.

TABLE 2

Calculation of Average Heats of Dissociation of Groups in Wool Dissociating at pH Values Above 6.

0°–25° C.			25°–50° C.		
Base bound per g. / millimoles	$-\Delta$pH	ΔH_0^{25}	Base bound per g. / millimoles	$-\Delta$pH	ΔH_{25}^{50}
0.1	0.75	11,190	0.1	1.47	25,820
0.2	0.81	12,070	0.2	1.04	18,310
0.3	0.85	12,640	0.3	0.84	14,800
0.4	0.88	13,100	0.4	0.78	13,720
0.5	0.89	13,240	0.5	0.84	14,800
0.6	0.83	12,380			
0.7	0.81	12,030			
	Average	12,380			

The numerical values of ΔH tabulated are very close to those, ranging from 10,000 to 13,000 calories per mole,[5] which would be expected to characterize the dissociation of hydrogen ions from the conjugate acid forms of amino or guanidino groups in amino acids. They are about twice as great as the values to be expected if the acidic dissociation of the hydroxyl group of tyrosine were being measured in any part of this region,[9, 34] and appear to support the suggestion made earlier[29] that the hydroxyl groups of tyrosine may not be titrated by base in the region of pH covered by this investigation. The values, although consistently slightly higher, are in fair agreement with the figure, 11,500 calories, found by Wyman for horse hemoglobin, and with an approximate value of 14,000 calories which may be deduced from the figures given by Pertzoff and Carpenter for casein.

The fact that the values for wool and for casein are so nearly equal to the heat of dissociation of water (13,481 calories at 25°[13]), shows that the effect of temperature on the amounts of base bound at any constant *hydroxyl ion* activities (as for example in a given solution of sodium hydroxide) would be very small. Thus, it is only because the amounts of base bound are compared on a scale of *hydrogen ion* activities that the very considerable temperature effect appears. It is the latter basis of comparison which has significance in terms of *acidic* dissociation constants, used consistently throughout this paper.

The degree of agreement with the results for other proteins may be construed as furnishing additional support for the validity of the corrections for alkaline hydrolysis of disulfide bonds included in the calculations of the amounts of base bound. Thus, if ΔH were calculated from the difference in the pH coordinates of the broken curves, representing the uncor-

rected measurements, very high values of ΔH (20,000–25,000 calories), entirely without precedent in investigations of amino-acids and proteins, would result. These values would not be independent of time, but would increase with increasing periods of exposure of the wool to alkali. Thus, only the values calculated from the corrected measurements and tabulated in Table 1 may be interpreted thermodynamically.

Regardless of what detailed significance may be attached to the values shown in Table 1, they are, in combination with the much smaller values characterizing the acid branch of the curve, entirely consistent with the view that the process of titration with acid consists in the replacement of hydrogen ions on the ionized carboxyl groups of the uncombined protein while the process of titration with alkali consists predominantly in the removal of hydrogen ions from the conjugate acids of the amino and guanidino groups.

2. Data Obtained At Constant Ionic Strengths

Although the data obtained in the presence of constant concentrations of chloride or potassium ions show a different functional relationship between the amounts of acid or base bound and pH,[2] the effect of temperature upon this relationship is so similar to its effect on the data obtained in the absence of salt that one may without further discussion tabulate representative values of ΔpH taken from figures 2 and 3, and the values of ΔH calculated from them. This has been done in Table 3.

It will be seen at once that the average of the values of ΔH calculated for the acid region of the curve for ~.2 *M* ionic strength in the temperature interval 0°–25° C (Table 3) is very close to the value 2380 given in Table 1 for this quantity in the absence of salt. The individual values fluctuate considerably but this is largely a consequence of the manner in which the freehand curve through the data has been drawn. In the higher temperature interval, 25°–50°C, there is practically no effect of temperature, just as in the data obtained with acid alone. The resemblance between these sets of data extends into the alkaline region, although here again there is great fluctuation among the individual values. It is possible that the drift from 11,000–12,000 calories, characterizing the middle portion of the alkaline curves, to 7000–8000 calories at their most alkaline end is a real phenomenon and represents transition at 0.5 to 0.6 millimole of base bound from the titration of amino groups, to the titration of tyrosine hydroxyl groups when more base is combined.* However, this supposition is not easily reconciled with the failure of a differential effect to appear in the measurements made in the absence of salt, nor with the expected relative strengths of tyrosine hydroxyl and arginine guanidino groups. An extreme fluctuation, resulting in a change of sign of ΔH, is found in the region of very small amounts of combined base. As in the data obtained without salt, this may be ascribed to the small slope of the titration curve in this region and the resulting large effect of ΔpH which slight changes in the drawn curves, or slight errors in corrections for ash, would produce. Wide fluctuations are also found in the data listed for the interval 25°–50° C but the average of the values given is 15,060 calories, in good agreement with most of the individual values in Table 2 for this temperature interval.

* Recent work in this laboratory on the combination of base by silk, in which most of the acidic groups are phenolic, indicates that the hydroxyl groups of tyrosine dissociate hydrogen ions in this region of pH values.

TABLE 3

Average Heats of Dissociation of Acidic and Basic Groups in Wool Calculated from Titration Data Obtained at Constant Ionic Strength.

Ionic Strength 0.2

Acid Region

0° C.–25° C.			25° C.–50° C.		
Acid bound m moles/g.	$-\Delta pH$	ΔH_0^{25}	Acid bound m moles/g.	$-\Delta pH$	ΔH_{25}^{50}
0.1	0.17	2540	0.1	0.03	530
0.2	0.17	2540	0.2	0	0
0.3	0.28	4170	0.3	0	0
0.4	0.26	3880	0.4	0	0
0.5	0.17	2540	0.5	0	0
0.6	0.11	1640	0.6	0	0
0.7	0.06	890	0.7	0	0

Alkaline Region

0° C.–25° C.			25° C.–50° C.		
Base bound m moles/g.	$-\Delta pH$	ΔH_0^{25}	Base bound m moles/g.	$-\Delta pH$	ΔH_{25}^{50}
0	0	0	0	0.34	5,990
0.1	−0.13	−1,940	0.1	1.31	23,100
0.2	+0.64	+9,540	0.2	0.95	16,710
0.3	0.75	11,180	0.3	0.82	14,430
0.4	0.82	12,200			
0.5	0.82	12,200			
0.6	0.58	8,650			
0.7	0.50	7,450			

Ionic Strength 0.5

Acid Region 0° C.–50° C.			*Alkaline Region* 0° C.–50° C.		
Acid bound m moles/g.	$-pH$	H_0^{50}	Base bound m moles/g.	$-pH$	H_0^{50}
0.1	0.17	1370	0	0.325	2,620
0.2	0.17	1370	0.1	1.84	14,820
0.3	0.15	1210	0.2	1.77	14,240
0.4	0.16	1290	0.3	1.67	13,470
0.5	0.15	1210	0.325	1.61	12,900
0.6	0.15	1210			
0.7	0.16	1290			
	Average	1280			

The data obtained at an ionic strength of 0.5 exhibit smaller fluctuations and are numerically in good agreement with the values for ΔH obtained in the other sets of experiments. The average value of ΔH_0^{50} in the acid region is only 1280 calories, but it has already been shown that practically all of the effect of temperature in the acid region is manifested in the lower half of this large interval of temperature. It is justifiable, therefore to use double this figure, or 2560 calories, as the value of ΔH_0^{25}, for comparison with the other sets of data. In the alkaline region the individual values of base bound between 0.1 millimole/g and 0.325 millimole/g are constant within the error of the measurements and are close to those found in the other sets of data. Owing to the large amounts of decomposition at this temperature, the measurements do not extend sufficiently far into the alkaline region to determine whether the apparent fall in the values of ΔH found at 0.2 ionic strength would be found in these experiments also.

3. Comparison with Calorimetric Data

It is of interest to compare the present estimates of 2380, 2600, and 2560 calories for the heat of dissociation of the carboxyl groups of wool in the temperature interval 0°–25° C with the experimental value for the heat evolved at 0° per equivalent of hydrochloric acid combined by wool, as determined directly by a calorimetric method by Speakman and Stott.[37] The value obtained by these authors was 3560 calories, significantly higher than our own figure. In calculating this quantity, Speakman and Stott assumed that there were only negligible differences between the titration curves of wool at 22.2° and 0°; this was done in order to estimate the amount of acid combined at each pH from a titration curve obtained at 22.2°. The error introduced by this approximation may easily approach 1000 calories in the calculated result when less than half the maximum amount of acid is bound. However, this source of error should be practically negligible when high concentrations of acid are used, since then the amount of acid combined is independent of small changes in pH and temperature. Under these conditions, the heat of dilution of the acid is also relatively large, and the heat of reaction, calculated as the difference between the heat of dilution and the total heat evolved, is subject to a larger uncertainty. Nevertheless, the values obtained with high concentrations of acid are probably not subject to an error of more than two or three hundred calories. They appear entirely consistent with the value reported here; the higher value of Speakman and Stott refers to 0° while the value obtained by the titrimetric method of the present paper is the average of a very low value at 25° and an appreciably higher value at 0°.

It should be pointed out that the measurements made by Speakman and Stott were not interpreted by these authors as heats of dissociation of the carboxyl groups, but rather as the heats of reaction of the *basic* (amino) groups with acid. Since the value obtained was very much lower than the value which usually characterizes the neutralization of a base by an acid, Speakman and Stott concluded that the value was so low as to indicate that the basic side chains of wool were not free but were combined with acid side chains to form salt linkages, as those authors had previously suggested. However, since wool is an ampholyte and in the uncombined form a dipolar ion as well, it is clear that the heat measured was not analogous to the heat of neutralization of a base by an acid, but to the heat of association of

hydrogen ions with carboxylate ions and that hence the results obtained provide no evidence either for or against the existence of salt linkages.* It is evident that calorimetric measurements of the heat of combination of wool with *base*, had they been made, would have led Speakman and Stott by the same process of reasoning to a different set of conclusions.

4. Significance of the Heats of Dissociation

The estimated values of ΔH reported in this paper have been calculated by assuming that when the pH values at which a fixed amount of base is bound at two different temperatures are compared, under certain conditions $\Delta pH = -\Delta \log K$. The justification for relating ΔpH to a change in the logarithm of a hydrogen ion dissociation constant characterizing a single set of dissociating (acid) groups in the conventional formulation of the dissociation equilibria for a dissolved protein has already been cited and discussed. It remains to enquire whether this method of analysis is equally valid for the theory of the titration curve of wool presented in an earlier paper,[29] which assumed that anions of the acids used, as well as hydrogen ions, are only partially dissociated from the protein.† In terms of this theory, the positions of the curves of acid combination, with respect to the pH axis, are determined not by log K, where K is a conventional hydrogen-ion dissociation constant, but, to a high degree of approximation, by log $K'_H K'_A$ where K'_H is the hydrogen-ion dissociation constant characterizing the equilibrium

$$WHCl \rightleftharpoons WCl^- + H^+ \qquad (2)$$

and K'_A is the constant characterizing the dissociation equilibrium

$$WCl^- \rightleftharpoons W^{\pm} + Cl^- \qquad (3)$$

in which $W^{\pm}$ represents wool in the uncombined state, and the other symbols have their familiar chemical significance. The position of curves obtained in the absence of salt is determined approximately by $\frac{1}{2}$ log $K'_H K'_A$ rather than by log $K'_H K'_A$.[29]

It is apparent therefore that in the presence of a constant anion concentration, ΔpH represents the sum of $\Delta \log K'_H$ plus $\Delta \log K'_A$. In the absence of salt it is approximately equivalent to one half of this quantity. Thus, the heat of dissociation calculated by inserting $-\Delta pH$ in place of $+\Delta \log K$ in the Van't Hoff equation is actually the sum of two heats of dissociation, associated with reactions (2) and (3).

It is of interest, therefore to determine what part of the total heat effect is to be attributed to each of the two consituent equilibria. An estimate of the distribution in the case of combination with acid may be made as follows: It has been shown that at high concentrations of chloride

* The values obtained by Speakman and Stott with monochloroacetic acid are essentially the same as with hydrochloric acid over the part of the titration curve in which the amounts of monochloroacetic acid combined at a given pH are the same as the amounts of hydrochloric acid combined, but much lower values of ΔH are obtained at high concentrations of the partially dissociated acid, when large excess amounts of acid are bound. This indicates that the heat of combination of wool with the *excess* acid is very low, or zero. Direct measurements of the heat of combination of this excess acid now in progress in this laboratory show that this is indeed the case.

† This theory, originally proposed to explain the large scale effects of the concentration of added neutral salts on the position of acid-combination curves for wool on the pH axis, has since received additional support.[30]

the position of the titration curve with respect to the pH axis is practically independent of K'_A. The effect of temperature on the midpoint pH of curves obtained under these conditions must therefore be attributed in its entirety to an effect upon K'_H. This effect has been estimated (Table 3) as some 2500 calories. Since the effect of temperature upon K'_H must be invariant, regardless of whether or not salt is present, a contribution to ΔpH in the absence of salt of approximately one half the amount found at high concentrations must be ascribed to the temperature effect on this constant. This contribution to ΔpH, about 0.08 units, also happens to be just half of the total effect of temperature (expressed as ΔpH) found when salt is absent. Since the remaining half of the pH shift produced by a change in temperature under these conditions must be ascribed to the effect of temperature upon K'_A, it is clear that the heats of dissociation of hydrogen ions and of chloride ions are approximately equal, and that the sum of the heat changes associated with the two sets of equilibria (2) and (3) is roughly double the values calculated from ΔpH under either set of conditions.

In drawing conclusions from a comparison of the numerical results obtained in this investigation, or by the calorimetric method of Speakman and Stott, with those reported for amino-acids and proteins *in solution*, a certain caution is desirable. The reaction of dissolved acid with a dissolved ampholyte involves only changes in heat content which may be described as heats of reaction and heats of mixing (the latter is small). The reaction of dissolved acid with wool involves in addition a heat change equivalent to a heat of adsorption or a heat of condensation in that quantities of acid are transferred from a large volume, that of the aqueous phase, to a small volume, that of the fibre.

Thus the total reaction may be separated into two steps

$$(H^+)_{aq} \rightleftharpoons (H^+)_{wool} \tag{4}$$

$$(H^+)_{wool} + WCOO^- \rightleftharpoons WCOOH \tag{5}$$

in which the first equation represents the transfer of ions to the wool phase, and the second represents the reaction of the ions with the groups in wool which combine with them. The heat effect estimated by substituting ΔpH for $\Delta \log K$ in the Van't Hoff equation represents the sum of the heat changes involved in the two equilibria represented in eqs 4 and 5 rather than the heat of dissociation corresponding to eq 5 alone. The latter can only be obtained by estimating, if posible, the heat change corresponding to eq 4 and subtracting it from the total heat. The magnitude of the heat of the transfer represented in eq (4) which is brought about at the expense of the chemical potential energy of the reactants, may be estimated by calculating the entropy change at equilibrium from purely geometrical considerations, if it is assumed that there is no important difference between the two phases with respect to the degree of interaction within them of the ions with one another, or with the solvent. This calculation may be made with sufficient exactness for the present purpose from the approximate relation

$$\Delta S = nRT \ln \frac{V_{aq}}{V_w} \tag{6}$$

in which n is the number of moles compressed into the volume of the wool phase V_w from the volume of the aqueous phase V_{aq}, and ΔS is the entropy change. This simplified equation leaves out of account the entropy change contribution from the dilution of the hydrochloric acid remaining in the aqueous phase at equilibrium, but when the acid is initially more dilute than 0.01 M, under the conditions of the present experiments, the final concentration is so low as to make this contribution small.* No distinction is made in this method of treatment between the molal entropy change between the initial and final states and the molal entropy change for an infinitesimal change at equilibrium, although it is only the latter which, multiplied by T, may be equated to ΔH in any actual system. In the present case only the entropy changes inherent in the dimensions of the system, and therefore only those characteristic of an ideal gas, are under consideration; therefore the two molal entropies cited will be identical.

Substituting in eq. 6 numerical values from representative experiments in which low initial concentrations of acid were used and which therefore correspond fairly closely to the standard state conditions at which ΔH is defined, the ratio $\frac{V_{aq}}{V_{wool}}$ becomes very nearly 100, and $T\Delta S$ ($= \Delta H$) at 0° C is approximately 2500 calories per mole of acid transferred. This figure is close to the figure calculated from the data in the acid region. Thus, the heat of dissociation of a hydrogen ion from a carboxyl group in wool in the temperature interval 0°–25° C, *exclusive of the heat of transfer of acid between phases,* may be very much less than the value reported here, and may even be negative, as in the corresponding values obtained by Wyman with horse hemoglobin.

The fact that the heats of dissociation obtained from the alkali-combination curves of wool are also somewhat higher than the corresponding values reported by Wyman is entirely consistent with this suggestion. A similar contribution to the effect of temperature on the pH coordinates of titration measurements must be expected in all heterogenous systems, whether they are of such a nature as to be amenable to treatment by means of the Donnan membrane equilibrium equations or require the type of stoichiometric anion-association analysis applied to wool protein by the present authors.

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Abstracts

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Address, Secretary's Office, 65 Franklin St., Boston, Mass.

I. Fibres (Synthetic and Natural) and Fibre Analysis

Anisotropy of Cellulose Sheet. D. G. Drummond. *Nature*, Jan. 13, 1940, V. 145, P. 67; abs. in *Eastman Kodak Abs. Bull.*, May 1940, P. 282.

The author shows that regenerated cellulose sheet is birefringent in a way which might reasonably be expected from extrapolation of Spence's results for sheets made from cellulose esters. The relative unimportance of side-chain orientation in cellulose itself results in a generally greater birefringence and a change in the "slow-ray direction" as compared with the ester films. Numerical results for regenerated cellulose sheets are given. (S)

Casein Fibres: Prevention of Sticking and Felting. *Rusta*, 1940, V. 15, P. 123–4; abs. in *J. T. I.*, July 1940, V. 31, P. A364.

Casein fibres, even after hardening with aldehydes, show a tendency to stick together and felt. They usually contain traces of mineral acid derived from the spinning and hardening baths. The fibres can be separated by washing with a dilute alkali solution, e.g., a solution of ammonia, sodium bicarbonate, caustic soda, or an organic base such as methylamine. After this treatment the fibres are washed, acidified and soaped in the usual manner. Suitable procedures are described. (C)

THE ECONOMIC VALUE OF A WOOL-TYPE RAYON STAPLE FIBRE. *Rayon Text.* Mo., May 1940, V. 21, P. 57–9.

The "wool-type staple fibre" discussed has the properties of the ordinary rayon staple fibre, plus the advantages of a wool feel, appearance, crimp and warmth, and is spun on cotton machinery. (C)

LECITHIN FROM SOYBEAN: ITS USES IN THE TEXTILE INDUSTRY. E. W. K. Schwarz. *Rayon Text. Mo.*, May 1940, V. 21, P. 63–4. (C)

NITRATED COTTON AND RAMIE FIBRES: STRUCTURE. G. Mangenot and Madeleine Raison. *C. r. Acad. Sci.*, 1940, V. 210, P. 674–676; abs. in *J. T. I.*, July 1940, V. 31, P. A395.

Microscopic observations of the dissolution of nitrated cotton and ramie fibres in cyclopentanone and di-ethylene glycol nitrate are discussed. The observations indicate the existence on the surface of cotton fibres of systems of fine fibrils in ring or spiral formation. The nitrated ramie fibres gave no evidence of ring or spiral arrangements of fibrils but broke up into long needle-shaped fragments parallel to the fibre axis, which dispersed and dissolved. (C)

NYLON FIBRE: OPTICS. A. Frey-Wyssling. *Nature*, 1940, V. 145, P. 821; abs. in *J. T. I.*, July 1940, V. 31, P. A397.

Although the diameter of Nylon fibrils is only about 19 μ they show interference colors of the third order. For the calculation of the double refraction their slightly elliptical cross-section must be taken into consideration; the large and small diameters can easily be measured under the microscope with slightly twisted fibrils. The double refraction of fibrils examined amounted to 0.060, n_α being 1.520 and n_γ about 1.580. These figures agree closely with those of silk fibroin and natural cellulose fibres (ramie). Stretched fibrils are strikingly photoelastic; the retardation may increase by 30% before the fibril breaks. (C)

SPONTANEOUS EXTENSION OF CELLULOSE ACETATE FILMS. E. Freund and F. Deutsch. *Rayon Text. Mo.*, May 1940, V. 21, P. 40–3.

This article discusses the phenomenon. When orientated acetate films containing residual solvents are treated with liquids under conditions suitable for the removal of such solvents, the films elongate as high as 100% without mechanical assistance. This "spontaneous extension" is retained upon drying. (C)

THE STRUCTURE OF CELLULOSE. W. H. Hayford, Jr. *Rayon Text. Mo.*, June 1940, V. 21, P. 55–6; July 1940, V. 21, P. 56–7.

Anhydroglucose units, linked together as in cellobiose, are connected into long chain molecules. The principal features of the cellulose chain molecule are tautomeric end molecules and the presence of the majority of the anhydroglucose units with three hydroxyl groups. The cellulose chains are united into bundles. The bundles combine to form fibres. In the fibre there is a regular recurrence of the atoms which give cellulose a crystalline nature. (C)

THE STRUCTURE OF CELLULOSE AND OTHER POLYMERS RELATED TO SIMPLE SUGARS. W. N. Haworth. *Chemistry and Industry*, Oct. 14, 1939, V. 58, No. 41, P. 917–25; abs. in *Eastman Kodak Abs. Bull.*, May 1940, P. 283.

A review is given of studies made on the degradation products of cellulose, starch, glycogen, inulin, and related products as a guide to the structure of the parent high polymers. (S)

II. YARNS AND FABRICS

BALDUS-PROSS SPINNING PROCESS: EXAMINATION. W. Oeser, E. Siefers and A. Tafazzoli. *Textilber., English Edn.*, 1940, V. 21, P. 30–33; abs. in *J. T. I.*, June 1940, V. 31, No. 6, P. A307.

Attempts to shorten spinning processes are discussed and an account is given of a study of the Baldus-Pross process. This process operates with two draw-frame passages; the first retains the usual six-fold doubling and six-fold draft, but drafting is increased to 14–15 in the second frame. A special trumpet is used to condense and smooth the fine sliver. The draw-frame sliver is then fed to a speed frame which, operating with drafts of the order of 4 to 7, produces roving from which yarn can be spun on the ring spinning frame on pull-through drawing heads with a single feed. Comparative tests of ordinary and Baldus-Pross methods have been made in the spinning of cotton and a staple fibre-cotton mixture. The results of sliver and roving regularity tests and yarn strength tests are tabulated and discussed. The causes of the inferior regularity of draw-frame slivers and roving observed in the Baldus-Pross process are discussed and the need for more careful attention to preparatory processes is pointed out. The conclusion is drawn that the Baldus-Pross process represents an improvement in spinning technique. Manufacturers' opinions of this process differ greatly, but it is generally held that the method may be quite useful for low and medium counts up to 20's. (C)

FABRICS: STRUCTURE. G. Vandorpe. *L'Industrie Textile*, 1939, V. 56, P. 432–434, 480–483, 526–528, 569–571; 1940, V. 57, P. 16; abs. in *J. T. I.*, June 1940, V. 31, No. 6, P. A336.

It is pointed out that a scientific study of fabrics must be based on a study of the weave employed and of the characteristics of the constituent yarns. The "hypothetical diameter" of a yarn, assuming the yarn to be a cylinder, is used as a basis for the study of the structure (number of ends and picks per inch or centimetre possible with the given weave and yarn count) of a fabric, the determination of this diameter is explained, and various fundamental weaves are studied in regard to the number of yarn diameters in a repeat. Practical applications of the theoretical work are discussed and illustrated by examples, and it is shown that the possible yarn densities in a woolen fabric can be detemirned from a knowledge of the weave, and of the count and strength of the yarn employed. The relation between the angles formed by the cords of certain weaves and the fabric structure, and the contraction of yarns on twisting are also studied. The purposes of the sizing operation and the possibility of eliminating this process, the relation between fabric structure and flexibility, the measurement of the flexibility of fabrics are briefly discussed. (C)

THE FINISHING OF STAPLE RAYON FABRICS AND FABRICS CONTAINING STAPLE RAYON AND OTHER TEXTILES. Asu Vendor. *Monatschr. Textil-Ind.*, V. 54, Fachheft 3, P. 82–4 (1939); *Chem. Zentr.*, 1940, I, P. 1124; abs. in *C. A.*, 1940, V. 34, Col. 4580.

A discussion of the control, spot, removal, desizing (glue, starch and linseed-oil sizes), washing, bleaching, mercerization, dyeing and brightening of colors. (C)

THE LOADING OF SILK (PHYSICAL PHENOMENA). D. Jonte. *Teintex*, V. 5, P. 92–7 (1940); abs. in *C. A.*, 1940, V. 34, Col. 4579.

Methods of prepg. the $SnCl_4$ soln. are discussed. Hydrolysis of the $SnCl_4$ forms HCl and deposits gelatinous $Sn(OH)_4$ on the fibres. Any unhydrolyzed $SnCl_4$ is later hydrolyzed in the washing. Some of the $SnCl_4$ forms addn. products with the $—NH_2$ groups of the fibres as evidenced by the presence of fibroin degradation products in the Sn bath. The washing step is discussed in detail. In silicate baths, absorption as well as adsorption of the silicic acid is important. Conditions regarding the use of silicate baths are detailed. The addn. of some emulsified oils or sulfonated oils increases the elasticity of the fibres. Loaded silks dye a weaker color than unloaded silks owing to the silicic acid gel absorbing the dye. Washing removes some of the gel. (C)

THE PRESENT TREND OF TEXTILE FINISHING. T. H. Roberts. *Am. Dye. Rptr.*, Aug. 5, 1940, V. 29, P. 396–99. (C)

PROGRESS IN THE TECHNIQUE OF THROWING RAYON YARNS. W. F. Macia. *Rayon Text. Mo.*, May 1940, V. 21, P. 60–1; June 1940, V. 21, P. 59–60; July 1940, V. 21, P. 57–8; Aug. 1940, V. 21, P. 39–40.

Progress in throwing depends on a thorough understanding of the properties of the base yarns, on knowing what is expected of the thrown yarns, and on the production of the qualities in the thrown yarn that are necessary to produce the qualities required in the finished fabric. (C)

PROGRESS IN THE TREATMENT OF ACETATE RAYON. K. W. Zachrich. *Zellwolle, Kunstseide, Seide*, V. 44, P. 397–9; *Chem. Zentr.*, 1940, I, P. 957; abs. in *C. A.*, 1940, V. 34, Col. 4579.

Linseed-oil sizes no longer give better results than other sizes. Water-sol. sizes should not be used, as their application has not yet been developed satisfactorily. Suitable sizes for acetate rayon are Bezet size Ac, Blufajo and Silkovan K powder. (C)

"SHIRLASTAIN" FOR IDENTIFYING FIBRES. *Text. Mfr.*, July 1940, V. 66, P. 284–5.

This stain for identifying fibres can also be used to determine the completion of silk degumming or the efficiency of desizing of viscose rayon or acetate. It was developed by the British Cotton Industry Research Association and made and supplied by Imperial Chemical Industries, Ltd. (C)

III. Chemical and Other Processing (Not Otherwise Classified)

The Absorption of Substantive Dyes by Cellulose from Solutions of Very High Dye and Salt Concentrations. S. M. Neale and W. A. Stringfellow. *J. Soc. Dyers Col.*, January 1940, V. 56, P. 19–21. (C)

Acid or Gas or Atmospheric Color Fading on Dyed Acetate Rayon Goods. Herbert R. Mauersberger. *Rayon Text. Mo.*, February 1940, V. 21, P. 71–3. (C)

The Action of Alkylene Oxides on Cellulose. L. G. Lawrie, R. J. W. Reynolds and D. Ward. *J. Soc. Dyers Col.*, January 1940, V. 56, P. 6–17. (C)

Atmospheric (Gas) Fading of Colored Cellulose Acetate. Charles A. Seibert. *Am. Dye. Rptr.*, July 22, 1940, V. 29, P. P363–P374. (C)

The Boiling-Out of Wool Dyeings. H. Roesti. *Mell. Textilber.*, V. 21, P. 122–3 (1940); abs. in *C. A.*, 1940, V. 34, Col. 4576.

Wool dyeings with certain acid colors, of which Neolan Green BL Conc. (I) and Fast Wool Blue B (II) are typical, show marked alterations in shade and strength on long boiling. This is attributed to the action of a reductive product formed by degradation of the wool. Oxidizing agents added to the bath tend to prevent this action but are themselves usually injurious to the dye mols. Dichromates, alums and chrome alums protect dyeings of I by virtue of their hardening action on the wool-fibre protein. With II they form undesirable ppts. HCHO, a coagulating agent for proteins, protects dyeings of I and II against boiling without adversely affecting shade or fastness properties. Formalin (2%) in the bath is recommended. (C)

Cold-Dyeing of Casein Fibre and the Determination of Casein Fibre in Mixtures. J. Lanczer. *Mell. Textilber.*, V. 21, P. 123–5 (1940); abs. in *C. A.*, V. 34, Col. 4575 (1940).

Casein fibre subjected to hot acid solns., as in the normal acid dyeing process, tends to lose HCHO and become hard and inelastic. Naphthol AS colors and certain sulphur colors can be successfully applied at low temps. These dyes are applied in alk. soln., and solns. with pH greater than 12 usually injure casein fibre. The addn. of Dekol and HCHO to the dye bath prevents the injurious effect of excess alkali. Sulphur dyes can be applied from a bath of $(NH_4)_2$ S contg. Dekol and HCHO. Casein fibre which has been treated with alkali couples directly with Fast Red Al Salt to give a reddish brown color. This point of differentiation from other fibres can be made the basis for a quant. estn. A weighed sample of the mixt. to be investigated is treated with alkali and then with an excess of standard Red Al Salt soln., which is subsequently back-titrated. The results are compared with those obtained from known mixt. by a similar procedure. (C)

THE COLORATION AND FINISHING OF TEXTILES WITH PIGMENTS. Julian Warwick. *Text. Col.*, July 1939, V. 61, P. 441–3; August 1939, V. 61, P. 533–35. (C)

DYEING ACETATE RAYON WITH ACID AND DIRECT DYES. P. M. Heertjes, C. Vogelsgang and H. I. Waterman. *Chimie & Industrie*, V. 42, P. 933–43 (1939); abs. in *C. A.*, V. 34, Col. 3920 (1940).

Acid and direct dyes can be applied to acetate rayon with the help of Al, Fe and Cr salts, and in some cases also with Zn, Cu and Co salts. Dyeing by the first 3 mentioned metal salts is due to an adsorption of the dye on the pptd. hydroxide. The optimum conditions are different for each dye, but they depend mainly on the quantity of hydroxide present. Ions such as sulfate can prevent adsorption, and the latter takes place between definite pH limits. The fastness of these dyeings to washing is not great, and the process cannot therefore be used for fabrics which are to be washed frequently. Generally speaking, deep shades cannot be obtained, even with the use of large quantities of dyestuff. (C)

THE DYEING OF CELLULOSIC MATERIALS: A REVIEW OF THE PHYSICS AND CHEMISTRY OF THE DYEING PROCESS. J. Boulton and T. H. Morton. *J. Soc. Dyers Col.*, V. 56, P. 145–59 (1940); abs. in *C. A.*, V. 34, Col. 4575 (1940).

A crit. review of studies of the fundamental processes of the absorption of substantive dyes by cellulose. Certain new data, relating to the imbibition of water by cellulosic fibres and to the kinetics of absorption of dyes by viscose rayon of round cross section and by the natural cellulosic fibres, are recorded. 67 references. (C)

THE DYEING AND FINISHING OF FABRICS CONTAINING RAYON STAPLE FIBRES. Harold DeWitt Smith. *Rayon Text. Mo.*, January 1940, V. 21, P. 84–5; February 1940, V. 21, P. 69–70; March 1940, V. 21, P. 43–4.

The properties of viscose and acetate staple fibres are compared with one another and with the properties of wool and cotton fibres. The principal steps of wet and dry processing in dyeing and finishing operations are then discussed with particular reference to the effect of the distinctive fibre properties on their behavior during processing and on the attainment of the desired characteristics in the finished fabric. (C)

THE DYEING OF MIXED ACETATE FABRICS AND YARNS. Richard Kahl. *Monatschr. Textil-Ind.*, V. 54, Fachheft 3, P. 77–8 (1939); *Chem. Zentr.*, 1940, I, P. 1109; abs. in *C. A.*, 1940, V. 34, Col. 4576.

Suitable treatments are discussed. Numerous substantive, diazotization, indanthrene, indigosol, acid, celliton, celliton fast and cellitazol dyes are listed which can be used for dyeing fabrics contg. acetate fibres mixed with cotton, staple rayon and wool. (C)

HANDLING HYDROGEN PEROXIDE: MODERN METHODS OF. Ralph L. Eriesson. *Am. Dye. Rptr.*, 1940, V. 29, P. P343–P345. (C)

IV. Research Methods and Apparatus

Analysis of Frequency Charts to Determine Quality and Performance of Textile Fabrics. J. Edward Gill, Jr. *Rayon Text. Mo.*, February 1940, V. 21, 73–75; March 1940, V. 21, P. 57–8. (C)

Density Determinations as an Aid in Examination of Fibres. P. M. Heertjes. *Chem. Weekblad*, V. 36, P. 610–11 (1939); abs. in *C. A.*, 1940, V. 34, Col. 4565.

An examn. of the d. of cotton in He-H_2O (6.25%) is actually fixed in the cellulose lattice and the remainder (about 20%) is adsorbed on the surface in the usual manner. (C)

Determination of Moisture in Native and Processed Cellulose. John Mitchell, Jr. *Ind. Eng. Chem.*, July 1940, V. 12, P. 390–1.

Moisture in various forms of cellulose is determined by cold extraction with methanol followed by direct titration for water with Karl Fischer reagent. The method is simple and precise. Recovery is more nearly complete than by the oven-drying techniques. (C)

Differentiation between Lanital, Wool and Casein. E. Justin-Mueller. *Rev. gén. mat. color.*, V. 44, P. 109–11 (1940); abs. in *C. A.*, 1940, V. 34, Col. 4579.

The properties of wool, lanital, egg albumin, and casein are tabulated: (1) after treatment with 8.5° Bé. NaOH at various temps.; (2) for biuret color reactions; (3) for color reactions using Na nitroprussiate to indicate S presence; (4) with the exception of albumin, for color reactions after concd. H_2SO_4, and followed by diln. with H_2O. No S is found in lanital. The hydroactivity of lanital can be diminished by the addn. of Ti oxide or Cr_2O_3. The biuret reactions of lanital and casein appear similar; the other reactions show little difference. (C)

Fulling Phenomena—A Simple Laboratory Method of Studying. George C. Le Compte and Joseph W. Creely. *Am. Dye. Rptr.*, Aug. 5, 1940, V. 29, P. 387–390, 408–09. (C)

Investigation of a Light-Aging Apparatus for Cellulosic Coverings. Jean Grard. *Pub. sci. tech. ministère air* (France), *Bull. services tech.*, No. 88, 11 pp. (1939); abs. in *C. A.*, V. 34, Col. 3923 (1940).

An app. is described contg. 2 daylight lamps (W wires and Hg arc) in a specially fitted Al chamber, under which the cellulosic material, such as airplane fabrics, is exposed on a revolving drum. The results of tests with this app. are compared with those using the Hg arc; by the former app. aceto-cellulosic materials are shown to be superior to nitro-cellulosic products. The Hg arc radiates certain wave lengths not found in ordinary daylight which are especially injurious to acetocellulose. (C)

Lustre in Fabrics. Thomas Lonsdale. *Silk J. & Rayon Wld.*, February 1940, V. 16, P. 15–16, 43.

Its definition is discussed; also instruments for its evaluation. (C)

MOISTURE METER FOR TEXTILE MATERIALS. E. H. Jones. *J. Sci. Instruments*, V. 17, P. 55–62 (1940); abs. in *C. A.*, V. 34, Col. 4583.

Many oven-dried textiles gain moisture on exposure to the air in such manner that a nearly linear relation exists between the log of the elec. resistance and the amt. of H_2O regained. An app. is described in which novel electrodes are used which avoid variations in resistance. A wide range of resistance is covered by interchangeable electrodes. The instrument employs common types of thermionic valves in a circuit so designed that simple adjustments can be made to correct for differences in the emission of valves and variations in voltage without altering the original calibration. Different electrodes are used for cotton and wool. The method does not apply to silk or acetate rayon which has very high resistance. (C)

A NEW PRACTICAL METHOD FOR THE DETERMINATION OF OXYCELLULOSE IN BLEACHING PRACTICE. Iosif Ionescu-Muscel. *Mell. Textilber.*, 1940, V. 21, P. 119–21; abs. in *C. A.*, 1940, V. 34, Col. 4582.

Like the widely used Schwalve method this detn. depends on the power of oxycellulose to reduce Fehling's soln. The sample is treated with an excess of Fehling's soln. and back-titrated with a standard soln. of invert. sugar. It is much more rapid (1.5 hrs.) than the S. method (27 hrs.), and gives consistently higher values for the Cu no. These values are correlated with the breaking strength of several tested samples. This method is suitable for control work in practical bleaching. (C)

A PROCEDURE FOR RAPID DRYING IN FIBRE ANALYSIS. P. Heermann. *Mell. Textilber.*, 1940, V. 21, P. 132; abs. in *C. A.*, 1940, V. 34, Col. 4578.

The app. is a small cylindrical metal container with ends of fine-mesh Cu-wire screen. The sample is exposed in it to a stream of warm air. (C)

THE STORAGE OF MOLD CULTURES. Wm. G. Chace. *Am. Dye. Reptr.*, Aug. 19, 1940, V. 29, P. 429–430. (C)

THE SURFACE FRICTION OF YARNS. A NEW INSTRUMENT FOR THE DETERMINATION OF THE COEFFICIENT OF KINETIC FRICTION. Lloyd W. Davis. *Rayon Text. Mo.*, February 1940, V. 21, P. 55–6; March 1940, V. 21, P. 59–62; April 1940, P. 71–2.

This method and instrument for evaluating the coefficient of kinetic friction of yarns against metal or other surfaces, fill a need created by high-speed processing. It is rapid, precise, simple in manipulation and economical in amounts of yarn required. With synthetic yarns, such as cellulose acetate, friction of yarn against itself may also be measured. Examples show some of the many uses of this instrument in the selection of yarn pretreatments and control of proper tensions essential to economical processing. (C)

TEXTILE TESTING LABORATORIES. Robert H. Brown. *Parks' Parables*, May 1940, Book 37, P. 1–13.

The importance of scientifically controlled atmospheric conditions in such laboratories is explained. (C)

V. Pure Science, Economics and Misc.

Analysis of Form Double Refraction. A. Frey-Wyssling. *Kolloid Z.*, January 1940, V. 90, No. 1, P. 33–40; abs. in *Eastman Kodak Abs. Bull.*, May 1940, P. 282.

The variation of the form double refraction with the refractive index of the medium surrounding the isotropic particles gives a hyperbola. In a mathematical analysis of this (Wiener's relation) it is shown that the angular orientation of the axis of the hyperbola varies with the relative volume of the medium. This angular axial variation is greater with negative, plate, form double refraction, than with positive, rod, double refraction. (S)

Bibliography on Flameproofing of Textiles. Emily Williams Akin, Prof. Lilly H. Spencer, and Dr. A. R. Macormac. *Am. Dye. Rptr.*, Aug. 19, 1940, V. 29, P. P418–P420; Sept. 2, 1940, V. 30, P. P445–P451. (C)

Cellulose Acetate: Structure. C. A. Redfarn. *Nature*, 1940, V. 145, P. 515; abs. in *J. T. I.*, June 1940, V. 31, P. A341.

Samples of cast plasticized secondary cellulose acetate sheet material have shown, with crossed nicols, a uniform yellow polarization color, indicating a considerable amount of orientation. If the casting flow lines, parallel to the "selvedge" edge, are taken as the direction of the *c* axis, the samples show oblique extinction. This phenomenon is consistent with the view that the cellulose acetate unit, and also the parent cellulose, is monoclinic rather than orthorhombic. (C)

Cellulose Sheet Swelling: Effect of Temperature and Concentration of Sodium Hydroxide Solutions. G. A. Richter and K. E. Glidden. *Ind. Eng. Chem.*, April 1940, P. 480–86; abs. in *Eastman Kodak Abs. Bull.*, July 1940, P. 383.

Cellulose sheets prepared from four different types of wood and from purified cotton linters were swelled in from 6% to 30% sodium hydroxide solutions at temperatures of from 5° to 35° C. The sheets were fabricated on a Fourdrinier-type machine. The weight and volume increases of the swollen sheets were determined after a standard draining procedure. In all cases the swelling was a maximum at from 10% to 12% sodium hydroxide, the maximum being more pronounced at the lower temperatures. (S)

Color Names: The ISCC–NBS Method of Standardization. Dorothy Nickerson. *Am. Dye. Rptr.*, Aug. 5, 1940, V. 29, P. P392–P396.

In order to promote uniformity of nomenclature in the presentation of textile color data, the Research Committee of the A. A. T. C. C. has endorsed the method of designating colors (known as the ISCC–NBS Method) developed for the Inter-Society Color Council at the National Bureau of Standards, and this paper is a description of the method. It was presented at the March 1940 meeting of Committee D–13 of the A. S. T. M. (C)

HUE SATURATION AND LIGHTNESS OF SURFACE COLORS WITH CHROMATIC ILLUMINATION. D. B. Judd. *J. Rsch. Nat. Bur. Stds.*, March 1940, P. 293–333; abs. in *Eastman Kodak Abs. Bull.*, July 1940, P. 382.

See *Monthly Abstr. Bull., 26:* 211, April 1940. (S)

MEASUREMENTS OF STRUCTURE VISCOSITY OF VARIOUS TYPES OF POTATO-STARCH PRODUCTS. H. Geinitz. *Kolloid-Z.*, 1940, V. 90, P. 58–65; abs. in *C. A.*, 1940, V. 34, Col. 3123.

The "Tsuda" viscometer (*C. A.*, V. 23, 10) was used for detg. the structure viscosity of dild. potato starch pastes. The starches were obtained from various types of com. potato flours. The effects of temp. and age of the pastes on the structure viscosity were measured. The viscosity decreased with increasing age of the paste, owing to purely chem. causes, mainly decompn. Increased temp. also lowered the viscosity. (C)

METHOCEL: PROPERTIES AND SUGGESTED USES IN THE PAPER INDUSTRY. R. M. Upright and F. C. Peterson. *Paper Trade J.*, May 2, 1940, P. 31–5.

Methocel, the water soluble methylcellulose of domestic manufacture, is a white fibrous solid which dissolves in cold water to give odorless, colorless, and nontoxic solutions. It is insoluble in hot water and organic solvents and unaffected by oily or greasy materials of animal, vegetable, or mineral origin. Aqueous solutions are neutral and resistant to alkali and dilute acids. When cold solutions are heated their viscosity decreases rapidly. Eventually a temperature is reached at which an increase in viscosity occurs, and within a few degrees the solution is transformed to a firm gel. Aqueous solutions of Methocel can be blended with those of starch, glue, casein, latex, dextrins, and water dispersible gums. Plasticizers may be added if necessary, those suggested being polyhydroxy compounds and invert sugar. Films deposited from solution onto paper are strongly adherent thereto and are hard, tough, and flexible. Paper when coated with a continuous methocel film, resists the penetration of oils and greases even at elevated temperatures. Quantities as small as 0.1–0.2 lb. per thousand square feet cause a marked increase in gloss of the printed or varnished sheet. The authors are associated with the Cellulose Products Div., The Dow Chemical Co. (C)

MICELLAR STRUCTURE OF CELLULOSE FIBRE. G. Centola. *Atti X° Congr. Intern. Chim.*, 1939, V. 4, P. 129–37 (in Italian); abs. in *C. A.*, 1940, V. 34, Col. 2169.

After investigating the acetylation of natural and mercerized ramie fibres, C. concludes: about 40% of the cellulose is in the amorphous state and acetylates rapidly without altering the dimensions of the cryst. portion of the fibre; under partial acetylation the amorphous portion can be recrystd. and proves to be cellulose triacetate; the mercerizing process increases the content of amorphous cellulose; the amorphous and the cryst. portions of cellulose are so intimately intermixed that not only a sepn. is impossible but not even a deformation of the partially acetylated cellulose can be noticed by the action of liquids which dissolve or swell cellulose acetate. The exptl. results confirm the "fringe micelle" hypothesis of structure for cellulose fibre. (C)